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.2.14	2.1.16	31.5.20
6.2.14	8.10.16	14-12-20
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Coal-Tar and Ammonia, by G. Lunge. Part 2.

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Pp. xiv, & from 563 to 1178 & 1 leaf adverts. Plates facing following pp. 882, 908, 996 & 1040, the figures they contain being including in Pagination of such. (no list). 1 Table to face p. 922. 1.12.13. 2.W.P.

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COAL-TAR AND AMMONIA

PART II

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COAL-TAR AND AMMONIA

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COAL TAR AND AMMONIA

PART II

CHAPTER IX

CARBOLIC ACID AND NAPHTHALENE

Carbolic Acid (Phenol)

For some years after the preparation of carbolic acid became an industry it was found suitable not to work for that purpose the whole of the "light oil," but merely the last portion (that between sp. gr. 0·980 or 0·990 and 1·000). Since then the demand for carbolic acid has largely increased, and that for naphthalene has risen to a considerable extent. Consequently all the principal factories manage their process so as to obtain a special fraction between that yielding the light hydrocarbons and the heavy oils, which is particularly rich in phenols and naphthalene. We have seen (pp. 366 *et seq.*) that this fraction is not made everywhere exactly on the same principles; and its quality at one works will consequently differ a good deal from that at another; but this makes no difference in the manner of treating it to the best purpose, which we shall now describe.

The fraction collected as carbolic oil, usually 7 or 8 per cent. of the total distillates, is run into tanks, where it is allowed to cool down, whereupon 25 or 30 per cent. naphthalene crystallize out, from which the liquid oil is separated in the usual way. This oil is of sp. gr. 1·0025 and a very thin liquid; it contains from 25 to 30 per cent. phenols, from 15 to 25 per cent. (according to the temperature) of naphthalene, and a little of the methylnaphthalenes and other compounds mentioned on p. 523 as found in the creosote oil. It possesses a characteristic "carbolic" smell.

Smaller tar-works usually sell the carbolic oil as such; others partially work it up into varnishes. Larger works

manufacture from it at least crude carbolic acid, if they do not proceed as far as the pure article.

The first operation is always redistillation in a light-oil still, constructed exactly like a tar-still, and holding about 5 tons. Sometimes it is provided with a dephlegmating-head 3 to 6 feet high, which simplifies the ulterior separation. The work is carried on like the first distillation of the tar itself, but is much easier, as no boiling-over need be apprehended, and lasts from twenty to twenty-four hours. At first a little crude benzol, say 6 or 7 cwt., comes over, together with the hydration-water of carbolic acid. When this is finished, the distillate is turned into the second receiver. The next period, during which the distillate should run in a jet about as thick as an ordinary lead-pencil, lasts six or eight hours, and about 3½ cwt. of water comes along with the oil. During this period the heating must be carefully regulated, to prevent boiling-over through a sudden liberation of hydrogen-water. When no more water comes over, all danger is passed, and the distillation can be carried on vigorously. Up to this moment the distillate is regarded as crude benzol and treated as such, as we shall see in the next chapter.

From this point the distillate is kept for carbolic acid, until a sample on cooling on a glass-plate shows a crystallization of naphthalene, at which point the thermometer indicates 215° or 220° C. This period lasts nearly ten hours, and yields about 55 cwt. oil.

At most works the distillation is interrupted and the residue run into the creosote-oil tank. At some places another fraction is taken, containing no more crystallizable phenols, but 40 or 50 per cent. cresols, which, after separating the naphthalene, is sent out as 40 to 50 per cent. carbolic acid, or else worked up into creoline or lysol (pp. 527 and 528). The residue from this can be employed merely for softening the pitch.

According to E. Waller,[1] in America the light oil is distilled at temperatures below 177° to 220°; steam is passed through the distillate so long as it carries away any oils; the distillate ("rectified coal-tar naphtha") is worked for benzol, and the residue ("naptha tailings") for phenol. If these short hints actually represent the American style of treating the first

[1] *Chem. News*, xliii., p. 150.

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coal-tar fractions, it cannot be pronounced quite so rational as it might be.

Experience has shown that carbolic acid proper (C_6H_6O) cannot very well be made from the creosote oils distilling above 240°. These always contain phenols, but mostly the higher homologues; and the latter are universally admitted to be of great importance in the process of preserving timber, being less soluble in water, and less volatile than carbolic and cresylic acids, so that it would seem wrong to remove them. We shall therefore not take the heavy oils into account for this purpose. On the other hand, if a "middle oil" has not been collected (from about 170°), in the working-up of the "light oil" (to be described in the next chapter), considerable quantities of residues rich in phenol and naphthalene are obtained; these are added to the "carbolic oil," and make it about equal to the "middle oil" of other works.

The following are examples of the composition of middle oils:—

Distilling at	I.	II.
	0	0 per cent.
100° to 180°	14·1	9·2 „
180° „ 200°	41·5	35·2 „
200° „ 250°	38·7	19·2 „

Watson Smith gives the following results for "light oils," really equal to "middle oils" from Wigan cannel-coal tar (*cf.* p. 412):—

Distilling below	Oil of sp. gr. 1·000.	Oil of sp. gr. 1·019.
	10	0 per cent.
180°	5	0 „
190°	12	5 „
200°	22	24 „
	49	29 „

Whichever way the fractionating is accomplished, the further work is conducted in a similar manner, to obtain the following products:—*Crystallized Carbolic Acid, Cresols, heavy solvent Naphtha, Pyridine bases, and Naphthalene.* We shall consider these *seriatim.*

Separation of Carbolic Acid and Cresols.

The first treatment of the rectified carbolic oil aims at the separation of the phenols from the indifferent hydrocarbons. The process originally proposed by Laurent[1] is essentially identical in principle with that which is employed at the present time. The fraction of coal-tar distilling between 150° and 200° is treated with a hot saturated solution of *caustic potash or soda*, some solid powdered caustic potash or soda is added, and the mixture well agitated. [In this detail, viz. employing solid caustic, the process differs from that at present in use; probably at that time, in 1831, the tar did not contain so much naphthalene as now, because the cast-iron gas-retorts then used could not be worked at such a heat as those now made of fireclay; moreover, Laurent worked with a comparatively low-boiling fraction, poor in naphthalene.] The oil sets to a crystalline paste; the liquid portion is decanted, and the solid part is dissolved in warm water. Two layers are formed—one light and oily (which is removed), the other heavy and watery (which is saturated with sulphuric or hydrochloric acid). The oil which is formed in the latter process and found floating upon the acid liquid is digested with fused chloride of calcium and fractionally distilled. Thus a white oily substance is easily obtained, which on being slowly cooled yields beautiful crystals.

It has been attempted to cheapen Laurent's process by employing lime[2] in lieu of potash or soda, boiling and strongly agitating. On settling, the neutral oils come to the surface and are removed by decantation; the lime-precipitate is decomposed by hydrochloric acid, and yields phenol. This simple and cheap process, however, does not give a good result; and the treatment with caustic soda is universally preferred, but with a much weaker solution than that prescribed by Laurent. At all events the preparation of perfectly pure crystallized carbolic acid is anything but simple and easy. It is said that such acid was first made on a large scale by Sell, of Offenbach;[3] but in

[1] *Ann. Chim. Phys.* [3], iii., p. 95.

[2] *Cf.* Hugo Müller, *Z. f. Chem.*, 1868, p. 270 (Runge had done this from the first).

[3] According to a private communication from Mr Brönner, of Frankfort, this gentleman as early as 1846 made so-called white limpid ("wasserhelles") creosote, which was frequently refused because in winter it solidified to a

any case it was introduced into trade on a manufacturing scale through the exertions of Crace Calvert and Charles Lowe, of Manchester, who for a considerable time had almost a monopoly of it. At the present day it is made at other English as well as continental works.

First of all it should be ascertained how much alkali the oil requires. It is not necessary in this case to make a formal analytical estimation (of which we shall speak hereafter), but only to find the minimum quantity of alkali required for exhausting the oil. This need only be tested for roughly, in the following manner:—50 c.c. of the oil is put into a 100 c.c. graduated cylinder; and the soda solution is gradually added, shaking after each addition and allowing the liquids to separate. The dark-brown solution of sodium carbonate is distinct from the oil which may be above or below it. The volume of the oil is noted; and if on the next addition of alkali it is not lessened, the last addition must have been sufficient. From this is calculated the quantity of alkali to be used in actual manufacturing work.

From what we have seen (pp. 215 *et seq.*) respecting the behaviour of phenol and cresol with alkalis, we know, first, that the lowest phenol, C_6H_5OH, that is, "carbolic acid" proper, is more easily soluble than its homologues, and hence requires a weaker lye; secondly, that a large excess of caustic liquor may reprecipitate the phenols. Still the margin is so large, that in regular manufacturing work a test like that just described is hardly required, because there will be no very striking differences in the percentage of phenol. But where unknown oils have to be treated, such a test will have to be applied.

Fractional saturation.—According to Behrens,[1] an important manufacturing "secret" for making crystallized carbolic acid consists in treating the oil with a quantity of dilute soda solution, insufficient for dissolving all the tar-acids; in that case carbolic acid, being the strongest, is first taken up. This is confirmed by G. E. Davis,[2] who treated light oil three times in

white crystalline mass! This was, of course, owing to the then general confusion between carbolic acid and the real, original "creosote" from beech-wood tar (*cf.* p. 209), which latter compound is never found in the solid state.

[1] *Dingl. polyt. J.*, ccviii., p. 363. [2] *J. Soc. Chem. Ind.*, 1893, p. 233

succession with one-third of the proper quantity of caustic-soda solution of 1·010, and who obtained crystallized phenol only from the first and second extraction, and nothing but cresols from the third.

It would appear (*e.g.*, from Kraemer and Spilker, in Muspratt-Bunte's *Chemie*, viii., p. 52) that this fractional saturation is also practised at several continental works, *e.g.*, in this manner. They analyse their crude oils and add to them only so much caustic liquor that it takes up nearly all the carbolic acid and but little of cresols; when acidified, it yields crude carbolic acid, solidifying at 25° to 30° C. The oils separated from the sodium carbolate solution are now treated with enough caustic soda solution to extract the higher homologues of phenol, and the last remaining oil goes to the creosote-oil tank.

The following special prescription for the extraction of phenol was given by Charles Lowe, the first manufacturer of the purest crystallized carbolic acid:[1] 20 tons of gas-tar are introduced into a retort and distilled. The first 200 galls. of "light benzols" are of no use for the extraction of carbolic acid. When that amount of distillate has passed over, the next 600 galls. are collected separately. For each 200 galls. of these oils, having a density of 1·0 to 1·005, 30 galls. of caustic-soda solution of sp. gr. 1·34 are added after dilution to 150 galls., and the oils are then agitated with the solution for two hours. The mixture is next allowed to settle for four hours, when the alkaline solution is drawn off and neutralized with sulphuric acid. The crude carbolic acid rises to the surface and is skimmed off, and is then allowed to settle in tanks for several days, after which it is ready for casking. The caustic soda used must be free from nitrates.

Here, as we see, rather dilute alkaline liquor is prescribed, In regard to this, the following points should be borne in mind:—The less pure the oils, the weaker should be the caustic solution, if good phenol is aimed at. With crude benzol (which always contains some phenol) stronger caustic can be employed; and the phenol obtained will be still better, though less in quantity, than that from carbolic oil. For this reason some distillers do not begin the washing of crude benzol, as usual, with sulphuric acid, but with caustic-soda solution of

[1] From Allen's *Commercial Organic Analysis*, 1st ed., p. 305.

sp. gr. about 1·200. In the case of "middle" or carbolic oil, such strong alkali would dissolve too much hydrocarbons, especially naphthalene, which would greatly impede the purification of carbolic acid, and might altogether prevent it from crystallizing. Moreover, oils are dissolved which have a tendency to turn dark in the air, and thus spoil the phenol. Hence in this case weak alkaline liquors must be employed; and probably Lowe's prescription is more trustworthy than any other, since his object is to obtain the best quality of crude carbolic acid from the tar-distillers.

Watson Smith takes 33 per cent. by volume of caustic liquor 18° or 19° Tw. for carbolic oil, or 40 per cent. by volume for light oil.

At a large English factory carbolic acid is extracted from all the light distillates, up to (of course not including) creosote oil, in the following manner:—The first runnings are treated with rather stronger caustic-soda solution, viz., of sp. gr. 1·15, and in great excess. This is done previous to the washing with vitriol. The solution thus obtained, containing some carbolic acid along with much free soda, is mixed with a fresh quantity of somewhat weaker alkali, so that the specific gravity descends to 1·125. This liquor is now employed for treating the carbolic oil, at a temperature of 65° to 77° C. The resulting solution of carbolate of soda is separated from the naphthalene oil floating on the top, and the latter dissolves also the impurities taken up by the caustic soda from the first runnings, which otherwise cause the carbolic acid, made from first runnings alone, to be of inferior quality. Thus, by simplifying the process, both the quantity and the quality of the carbolic acid are improved.

A large South German manufacturer states[1] that he obtains crude carbolic acid (with 50 per cent. crystallizable acid) by employing caustic liquor of sp. gr. 1·26, steaming the solution, and decomposing the alkaline liquor by acid. He lays much stress upon the subsequent fractional distillation of the crude acid, but none upon the employment of weak alkaline liquor, or upon fractional saturation (p. 569).

Where only crude carbolic acid is made, and no special conditions are imposed by the buyers, sometimes stronger

[1] In a private communication to the author.

alkaline liquors, up to 35 Baumé (=sp. gr. 1·32), are employed; but this must yield a product difficult to refine.

Knights and Gall (B. P. 5824, of 1887) agitate carbolic or middle oil with a mixture of cream of lime and solution of sodium sulphate. On settling, two layers are formed, the lower one being a solution of sodium carbolate in water, which is run off. The top layer consists of tar-oil, calcium sulphate, and a little solution of phenols; after passing through a filter-press, some more of the phenol-sodium solution can be separated. The latter is decomposed with sulphuric acid, and the sodium sulphate formed is used over again as before. In lieu of lime, any other alkaline earth, and in lieu of sodium sulphate, potassium sulphate can be used.

Staveley[1] proposes a similar process for the manufacture of sodium or potassium carbonate from the sulphates or sulphites, and states that, especially when employing phenols free from hydrocarbons, up to 96 per cent. of the sulphate or sulphite can be decomposed. He slakes about 11 cwts. of quicklime, and makes it into about 2 tons of cream of lime. When this is nearly cold, about 20 cwts. of phenols, boiling between 190° and 250°, or a corresponding quantity of tar oil, is added. The mixture is slowly run into a warm solution of 30 cwt. of sodium sulphate in about 4 tons of water, contained in a heatable pan provided with an agitator. The temperature of this mixture is kept at 30° or 40°, and the agitation is continued for an hour after finishing the addition of the calcium phenolate. After the mixture has settled down, 70 or 75 per cent. of the sodium phenolate solution can be got by decantation. The remainder is passed through a filter-press or a vacuum-filter, the residue is washed with about 3 tons of water, and the washings employed in the next operation as a solvent for sodium sulphate. If tar oil is employed in lieu of distilled phenols, a certain portion of the oil and of the phenolate is retained by the gypsum.—The solution of sodium phenolate is thoroughly carbonated with lime-kiln gases, and the phenols which separate out are run off after a few hours' settling. The solution of sodium carbonate, containing about 1 per cent. phenols, can be evaporated and the soda-ash calcined as usual. In order to recover that small quantity of phenol, a correspond-

[1] *J. Soc. Chem. Ind.*, 1888, p. 807.

ing quantity of caustic-soda solution may be added before the evaporation. In this case the phenol accumulates in the mother-liquor, which is again added at the close of a new operation, to avoid the presence of free caustic lime, which impedes the settling.

The same process, but extended to di- and trioxybenzene, oxynaphthalenes, and dioxyanthraquinones, has been patented by Landshoff and Meyer (Ger. P. 48270). They state that the reaction takes place most easily with alkaline sulphites, less quickly with the sulphates.

The Chemische Fabrik Ladenburg (Ger. P. 147999) also employs hydrated lime for separating the phenols from the neutral oils. The lime is added at the ordinary temperature, the solution of neutral calcium phenolates is separated from the oils by settling and distilling below 70° C. at reduced pressure, and is decomposed by heating above 70° into a mixture of basic phenolate and free phenol from which the latter is expelled by steam distillation. The solution of basic phenolate after cooling down, is used for extracting free quantities of tar oil, or is decomposed by an acid. (This patent was abandoned in 1906.)

We do not know whether any of these processes are anywhere employed in actual practice. Probably the great majority of works employ Laurent's process, with the modifications above described.

The mixing of carbolic oil and alkaline liquor must of course be done very thoroughly, and with gentle heating, say to 40° or 50°, by means of a steam-coil or jacket. Probably all larger works employ mechanical means for mixing. At some it is done by pumping both liquids continuously backwards and forwards, from a lower tank into a higher one and *vice versa*. At others they employ horizontal cylinders covered by a bad heat-conductor, with a longitudinal shaft and agitating-blades. Horizontal agitating-shafts have the drawback that they must pass through the sides of the vessel, in stuffing-boxes; but the agitation caused by them is more thorough than that produced by vertical apparatus. One of the best forms of the latter is that of a perforated piston moving up and down.[1] We shall treat of mechanical mixers more in detail in the 11th Chapter. At some places the agitation is effected by blowing in a current

[1] Hübner, *Dingl. polyt. J.*, cxlvi., p. 421.

of air, divided by a cross of pipes with many holes, or a perforated plate. This principle has the advantage of dispensing with all working parts within the liquid, and thus being equally applicable for acids and alkalis; the blowing can be performed by the same small blowing-engine which is employed at most tar-works for pumping the liquids by air-pressure, but it is

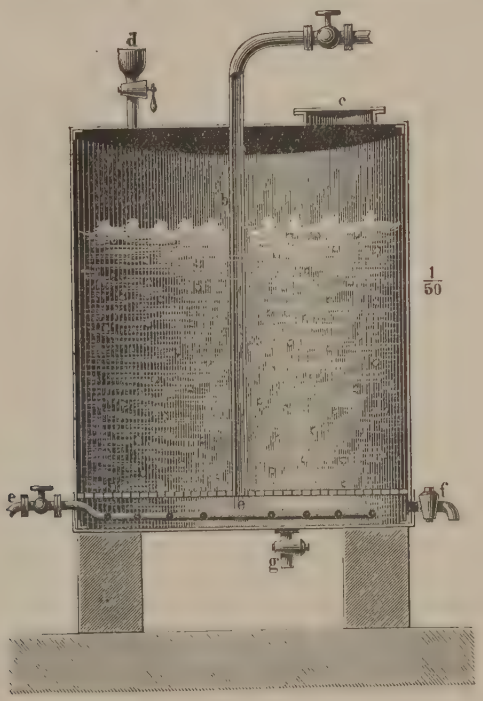


FIG. 153.

asserted that the carbolic acid extracted in this manner, owing to the action of the air, is more inclined to reddening than otherwise. Fig. 153 shows this arrangement. *a* is a perforated false bottom, which serves for dividing the current of air, blown in through *b*, into numerous jets; *c*, manhole; *d*, funnel and tap for charging with oil and alkali; *e*, steam-coil; *f*, discharge-cock a little above the bottom; *g*, another discharge-cock in the bottom itself. The air-blast must be so regulated that the

liquid shall not be splashed about, but only made to well up thoroughly. Instead of employing a plain cylinder, as shown in Fig 153, it seems preferable to make the bottom cone-shaped, or to give to the whole vessel the form of a truncated cone, at the lowest part of which the inlet pipes for air and steam are situated. A detailed paper on the application of compressed air for the pumping and mixing of liquids has been published by Ramdohr.[1]

According to Watson Smith, the oil and alkali are mixed up for an hour and a half; the mixture is then tested by mixing, in a 200 c.c. graduated cylinder, 140 c.c. of the alkaline liquor with 84 c.c. strong sulphuric acid, and allowing it to subside; unless at least 10 or 12 per cent. crude carbolic acid is found to collect at the top, the mixing should be continued.

The mixing-vessel for this purpose is always made of iron, usually wrought iron, which metal resists the liquor better than any other; the steam-coils, air-pipes, etc., are also made of iron. When mixing by an air-blast, the vessel should be only two-thirds full, on account of the frothing up. It is mostly closed by a wooden or iron cover, to minimize volatilization. According to the size of the works, the settling (which occupies several hours) will either take place in the same vessel, or else the whole contents will be run into a special vessel, placed at a lower level, so that the mixer can be charged again at once. The settling-tank must have two (iron) discharge-cocks, one in the bottom itself, another in the side a little above the bottom. The unchanged oil always floats on the alkaline liquid, which sometimes doubles its bulk and is of intensely dark brown colour. First of all this liquid is run off by the bottom cock, which is closed as soon as any traces of oil appear. Now the upper cock is opened, through which oil entirely free from alkali can be drawn off, whilst between the two cocks a layer of both liquids remains, which is best left behind in the vessel and worked up with the next charge. This is facilitated by making the bottom of a conical shape.

As stated by Watson Smith, the point at which the alkaline liquid is going to change for the oily one can be safely recognized by the turbid, milky appearance which sets in.

If is imperative to keep the alkaline liquid as pure as

[1] *Dingl. polyt. J.*, ccxvi., p. 158.

possible from the separated crude naphtha, because even a small admixture of the latter (especially of the naphthalene contained therein) afterwards prevents the crystallization of the carbolic acid. Hence great care must be taken in settling and in drawing off.

The *oil drawn off from the solution of sodium phenolate* (crude naphtha) contains some of the higher homologues of benzene and naphthalene (according to K. E. Schulze, *Berl. Ber.*, 1887, p. 409, 15 per cent. trimethylbenzenes, 15 or 20 per cent. tetramethylbenzenes, 15 or 20 naphthalene, and a paraffin melting at 20 C.), with pyridine bases. It furnishes principally naphthalene, pyridine bases, and solvent naphtha of various degrees. If naphthalene is not wanted, this oil is usually run to the "light oil" (*cf.* next chapter) and worked up therewith. Sometimes this does not pay, viz. when the original oil has been collected later on in the distillation; then the residues are run to the creosote oil. Where naphthalene is an object, this oil is by far the best raw material for it, as we shall see below.

This oil also contains benzonitrile or sodium benzoate formed from this (*cf.* pp. 209, 239), and can be treated for the recovery of benzoic acid as described in the patent of the Aktien-Gesellschaft für Teer- und Erdöl-Industrie, Ger. P. 109122. It is heated with caustic-soda liquor of sp. gr. 1·4, as long as any ammonia is given off. On cooling, the residue separates into an aqueous and an oily portion. The former is saturated with CO_2, the phenols separating thereby are removed, and the residue is now a pure solution of sodium benzoate, from which benzoic acid is obtained as a precipitate of fine, white crystals by adding some stronger acid.

The *liquor containing sodium carbolate*, to which is regularly added that obtained in the washing of benzol and light oil, may be at once decomposed by acid. But some prefer to interpose a special treatment for the *removal of impurities*. Thus Vincent[1] adds to the liquor 5 or 6 times its bulk of boiling water, to precipitate the dissolved hydrocarbons. This should not be overdone (*cf.* p. 217); and anyhow the success of this operation will depend upon the fact whether more or less concentrated alkali has been employed from the first. (Vincent starts with

[1] Payen, *Précis de Chimie industr.*, 6th ed., ii., p. 961.

concentrated alkali.) Schnitzler[1] recommends, as extremely efficient, heating the dark liquid in a copper still over a strong fire till the distillate (consisting of water, naphthalene, oils, and phenol) turns milky; the thermometer will then stand at 170°. Most of the phenol remains with the soda as a mass solidifying on cooling. It is dissolved in water in the still itself, and is diluted to three times the original bulk. After some days a mud is deposited, from which the clear liquor is separated. The latter is decomposed by dilute sulphuric acid; and the phenol separated is distilled from a glass retort. After putting aside the water "coming over at first, colourless liquid phenol of honey-like (?) smell was obtained, which solidified on the addition of a small piece of calcium chloride, or a crystal of carbolic acid. The portions passing over last were faintly yellow, and contained more liquid parts. The crystals, after draining them with a Bunsen pump and pressing them between paper, remained white for months in a stoppered bottle in moderate daylight; in an open glass they soon turned pink, and at last deliquesced to a yellow-red liquid. The colour was evidently produced by particles of dust floating in the air" (? see below).

For the large scale Schnitzler recommends a wrought-iron still with a block-tin, lead, or copper worm, and to put a second delivery-tube lower down for use in the later stage of distillation. Insufficiently heated sodium carbolate yields yellow, unpleasantly smelling phenol; it is essential to completely remove the colouring impurities by evaporation or carbonization, etc. An experiment with calcium carbonate did not succeed (perhaps because there was an excess of lime); the mass turned spongy, conducted the heat badly, and retained tarry matters and naphthalene.

Another purifying process is described in Stohmann-Kerl's *Chemistry*.[2] The crude sodium carbolate is run into open wood tubs, on the bottoms of which is laid a steam-coil perforated with many holes. The liquor is moderately warmed; and enough freshly prepared cream of lime is added to make the whole milky white. During this operation the mass is worked up with a wooden rake; and the heating is continued for twelve hours. After a few hours a skin appears on the surface, which

[1] *Dingl. polyt. J.*, ccxiv., p. 86. [2] 3rd edition, vi., p. 1181.

gradually turns into a red foamy scum. It consists of the naphthalene left in the liquor, mixed with lime. It is carefully removed with a perforated wooden scoop, either at once, or at least after the liquor has cooled down. Thus all naphthalene, even to the last trace, can be removed; but it is most essential to keep the heat at the right point. The temperature must never rise so high that the liquid wells up strongly. Perhaps an insoluble compound of lime and naphthalene is formed; but the action of the lime may be only mechanical, the naphthalene being secreted from the alkaline liquor as it is diluted by the steam blown in. In any case the tubs must be left uncovered and must stand in a cool room. When the naphthalene has been completely removed and the liquor has settled, it is carefully drawn off from the lime remaining at the bottom, and is decomposed by sulphuric acid.

The following process is now generally employed for the previous purification of the liquor:—It seems to be efficient and indispensable for obtaining good crude carbolic acid (free from dissolved or finely suspended hydrocarbons, a very slight admixture of which afterwards impedes the crystallization of phenol) that a current of steam is passed into the liquid, contained in an iron still provided with a refrigerator, till a sample of the distillate is perfectly clear and bright, without any milkiness.

The stills employed for this purpose are usually worn-out steam-boilers or tar-stills, of a capacity of 5 tons and upwards, provided with a fire-grate and an open steam-pipe, as well as a cooling-worm for the vapours. At first they are heated by an open fire, until the distillate is entirely free from oil, but even after several days' firing the water coming over has still a disagreeable smell. This is only removed by finishing the operation by blowing in direct steam during six hours; before doing this, the manhole is opened, so that the steam escapes into the air.

The solution of sodium carbolate in the still is now a dark liquid, entirely soluble in water, except a few floating solid particles, consisting of empyreumatic substances, which must be removed by filtration before separating out the carbolic acid. The only distillate collected during the operation is worked for naphtha and pyridine bases, as we shall see.

Now follows the *decomposition of the alkaline solution of*

phenols by mineral acid, and the separation of crude carbolic acid. This operation is generally performed in a wooden vessel lined with lead, which may be provided with a mechanical agitator; but in this case mixing by hand is easy and simple. Kraemer and Spilker (*supra*, p. 569) state that iron vessels may be employed, as the reaction is first alkaline, then neutral; but lead-lined vessels are preferable, as in this case a slight excess of acid does no harm. Sometimes this tank is covered over, so that any noxious gases escaping in decomposing the sodium phenate by acids can be conveyed under a fire and burned. The acid employed for the decomposition is mostly *sulphuric acid.* The solution of sodium sulphate resulting from this is probably never utilized as such; and the spontaneously crystallizing Glauber's salt is also of very small value.[1] If dilute caustic liquor and sulphuric acid of 140° Tw. be employed, but little will crystallize out spontaneously. Some tar-distillers take strong oil of vitriol (sp. gr. 1·84); but this is worse than useless, as sulphophenols are formed, which in the subsequent distillation decompose and carry sulphurous acid into the carbolic acid. The addition of the vitriol must be cautiously done, to avoid strong heating, and is only continued till the reaction has become distinctly acid. The men can tell this from the change of colour, without applying litmus-paper. According to Watson Smith, 1000 gallons, treated with 400 gallons of caustic-soda solution of sp. gr. 1·090, require about 22½ gallons of sulphuric acid of sp. gr. 1·74.

It has been several times attempted to replace sulphuric acid by the "acid tar," formed in washing the light tar oils (Chapter XI.), after depriving it, by dilution with water, of most of its tarry parts. But it is still very impure; and its use for decomposing sodium phenate has been given up everywhere, as the saving of acid does not compensate for the contamination of the phenol. It is true that another motive was the desire to get rid of that acid refuse; but the proposal of E. Kopp, to combine the employment of this refuse acid for decomposing the sodium phenate with working-up the resulting solution for the bases contained in coal-tar, could hardly be expected to meet with success, looking at the deterioration of the carbolic

[1] According to Watson Smith, the crystals always turn blue on standing in the air.

acid. We shall see in the next chapter that this "acid tar" is now generally worked up for the recovery of the pyridine bases.

According to Watson Smith, in Lancashire even fresh sulphuric acid made from pyrites is not employed for this purpose, but brimstone acid almost exclusively. [This is probably from an unfounded prejudice; for the reason, given in the *J. Soc. Chem. Ind.*, 1882, p. 342, that pyrites acid discolours the sodium sulphate, cannot hold good here, as the value of the crystallized sodium sulphate is almost nil, and certainly much less than the difference in price between pyrites acid and brimstone acid; moreover the sodium-sulphate solution is nearly always run to waste.] He further mentions that attempts had been made, but unsuccessfully, to replace sulphuric acid by *hydrochloric acid*, which is cheaper [and causes less trouble by crystallizing salts]. The alleged reason of this failure is that chlorides of ammonium and organic bases are formed, which later on are decomposed, and action upon the iron of the stills ensues; the ferric chloride distils over, and makes the carbolic acid dark and dirty. Ammonium sulphate produces no such consequences. Against these statements must be placed the fact that some of the best German works employ hydrochloric acid, and among them are those that turn out the very finest quality of white crystallized carbolic acid.

Lowe and Gill[1] propose decomposing the alkaline phenol solution by *sulphurous acid*. The aqueous solution of the bisulphite formed in this operation is either to be evaporated for crystallization, or employed for preparing sulphurous acid again. It is probable that this plan answers well; and the sulphurous acid would be obtained very cheaply by working-up the "acid-tar" from the washing of crude naphtha (*cf.* this in Chapter X.). But H. Köhler[2] has shown that no saleable bisulphite can be made from sodium phenolate, since the SO_2 from "acid-tar" is too much contaminated with empyreumatic substances. Moreover, the "acid-tar" is more advantageously employed for recovering the pyridine bases. But he found, at least in the laboratory, that the SO_2 can be purified by suitable means, such as adding sulphuric acid, creosote oil, wood charcoal, etc., before passing it into the solution of sodium phenolate, by

[1] B. P. 1453, 1880. [2] *Carbolsaure*, etc., Berlin, 1891, p. 33.

means of a Korting's injector. The solution of sodium sulphite thus formed might be decomposed by caustic lime, thus recovering caustic soda, and calcium sulphite, to be used as such or for the recovery of SO_2. This process might also be combined with that of Knights and Gall (p. 571), by employing the sodium sulphite solution, mixed with caustic lime, for the extraction of fresh quantities of carbolic acid.

Köhler (*Carbolsäure und Carbolsäurepräparate*) found that *nitre-cake* (acid sodium sulphate, with about 30 per cent. free SO_3) can be very well employed for decomposing the sodium phenolate, either in solution or in the state of fine powder. This is especially advantageous where calcined sodium sulphate (salt-cake) can be cheaply made from the crude Glauber's salt crystallizing out in the process.

In the place of strong acids, *carbonic acid* can be employed for decomposing sodium phenate. In Scotland this process seems to have been used for some years;[1] Brönner,[2] of Frankfort, had previously used it many years ago. A patent has been taken out by Clift (B. P. 967, of 1880) and another by Wischin (B. P. 3750, of 1880) for exactly the same thing.

The CO_2 used for this purpose need not be anything like as pure as that required for other purposes, *e.g.*, for making soda by the ammonia process. It is quite sufficient to make it by the action of limestone and coke (not coal; of course the CO_2 must be free from bituminous substances) in a cupola furnace, and purifying the gas from dust and also from SO_2. This can be done by passing the gases through a shaft filled with lumps of limestone, kept moist by a current of water. Since, anyhow, a pump is used for moving the current of gases, there is no difficulty in this process. The purified gas, which is under a pressure of $\frac{1}{4}$ to $\frac{1}{2}$ atmosphere, is now passed into the sodium carbolate liquor by means of a perforated pipe, lying at the bottom of the tank.

If the decomposition can really be completed without wasting too much carbonic acid (and this can be achieved by employing two or three vessels in succession, so that up to 90 per cent. of the CO_2 is utilized), there are considerable advantages gained by this process as against the employment of strong acids. In the former case the soda is not lost, as in the

[1] Mills, *Destructive Distillation*, p. 17.

[2] Private communication to the author.

latter, but is recovered as carbonate and can be used over again after causticizing. There would not, as now, be a rather considerable amount of phenol lost, either dissolved or suspended in small drops, in the solution of sodium sulphate or chloride; for as the liquor is causticized and used again, the phenol would be recovered. No washing of the phenol would be at all necessary, as the latter would retain no mineral acids, which probably give rise to the formation of traces of rosolic acid (p. 220), and thus turn the carbolic acid red.[1] This, of course, presupposes that the carbonic acid itself is entirely free from stronger acids, which is hardly the case in the ordinary way of working, since even that made from coke or in lime-kilns is contaminated with sulphurous acid. It seems, therefore, necessary to wash the CO_2 most thoroughly with water, or else to produce it by the action of superheated steam on limestone in iron retorts. Lest too much of it should be wasted, it should be divided into numerous jets by a perforated false bottom or the like, and several vessels should be employed in rotation to utilize the gas methodically, so that the fresh gas (which in the case of lime-kiln gases contains upwards of 30 per cent. CO_2 by volume) shall always be brought into contact with nearly saturated liquor, and the poorest gas with fresh liquor, on the same principle as that in accordance with which black ash is lixiviated.[2] There would also be this advantage, that, as the carbonic acid need not in this case be free from oxygen, any fire-gases might be used, if well washed: oxygen even acts advantageously here (*vide infra*).

J. Hardman (B. P. 7079, of 1885) runs the alkaline solution of the phenols down a coke tower, in which ascends impure carbonic acid, namely, the gases from the manufacture of ammonium sulphate, after having been freed from sulphide of hydrogen by oxide of iron. This inventor also utilizes the suggestion (already mentioned in the first edition of this

[1] According to Dr Kraemer (priv. comm.) the reddening of phenol is caused by benzoic acid, contained in the crude phenol, which passes over in the distillation and takes up some iron from the cooler. The ferrous salt thus formed is converted into ferric salt by the oxygen of air, and this produces the red colour.

[2] This is described in detail in my treatise on the *Manufacture of Sulphuric Acid and Alkali* (Gurney & Jackson), 2nd ed., vol. iii., pp. 235 *et seq.*

treatise, 1882) to recausticize the alkaline carbonate formed, and thus save the 2 or 3 per cent. of tar-acids otherwise lost with the sodium-sulphate liquors. According to G. E. Davis (*J. Soc. Chem. Ind.*, 1893, p. 233) this process is still regularly in use at Hardman's works.

Some experiments made in my laboratory[1] seem to show that the separation of phenol from its salts by means of carbonic acid is complete. It may also be stated that difficulties which formerly caused some manufacturers to abandon this process, after trying it for a while (*cf.* the last edition of this treatise, p. 494), have been overcome, and it can be recommended without any hesitation.

Sulphuretted hydrogen has also been proposed for decomposing the carbolate of soda (Jane, Elland, and Steuart, B. P. 2469, 1883). Since the patent was annulled, owing to the neglect of filing the final specification, there does not seem to be much in it.

After the separation of the crude carbolic acid, the solution of salt, if sulphuric acid has been employed, must be drawn off hot, lest it crystallize in the precipitating tank. In the case of hydrochloric acid there is no such danger, and more time can be given for the solutions to clear, so that less phenol is lost with the solution of salt. The latter is drawn off by a tap in the bottom, which is shut the moment any carbolic acid appears, whereupon the latter can be drawn off in the pure state from another tap higher up. It is preferable to leave the carbolic acid to itself for a day or two to clear, so that the salt solution suspended in it may completely separate at the bottom: this can be done in a special settler. The longer the time given for the salt solution to separate from the carbolic acid, the better for the quality of the latter.

In many cases the crude carbolic acid is now sold as such; in other cases it is washed once or twice with water to remove the mineral acids—which, however, is never done completely, because the washings would carry away too much carbolic acid. In any case the washings should not be thrown away, but employed for dissolving the caustic soda. The washings are found floating on the top of the carbolic acid, and are run off best by a drop-siphon (Fig. 154), which can be gradually turned down. This is much more convenient than a common siphon.

[1] *Chem. Zeit.*, 1883, p. 29.

Sometimes the crude carbolic acid is previously *distilled* by the tar-distiller, in order to get it up to the requirements laid down by the buyers (*cf.* below). In that case the fraction distilling between 175° and 205° or 210° is collected as crude carbolic acid. The fraction below this goes to the light oil, the residue to the creosote oil.

Crude carbolic acid should have a specific gravity of 1·050 to 1·065 at 15°·5. In the presence of light tar oils its specific gravity is often only 1·040 to 1·045. It contains phenol, the different isomeric cresols, phlorol, xylenol, neutral tar oils, naphthalene, empyreumatic substances of unknown character, and water. The processes for testing its percentage will be described later on.

FIG. 154.

The *waste-water* running away in carbolic acid manufactures generally contains traces of that acid, which are very troublesome when that water gets into a public water-course; even its treatment with lime does not quite remove the smell. Weigelt and Mehring (*Chem. Ind.*, 1904, p. 596) propose effecting this by treating the waste-water with ozonized air, but this is probably too expensive in ordinary circumstances.

The Manufacture of pure Crystallized Carbolic Acid.[1]

Crude carbolic acid contains cresols, water, resinous matters, etc. The *water* is easily removed by distillation; it passes over almost entirely at 100°, whereupon the boiling-point rises rapidly, and at 180° anhydrous phenol passes over. Bickerdike[2] had recommended the addition of 1 or 2 per cent. dehydrated cupric sulphate, but on the large scale the removal of the water is exclusively effected during the various redistillations.

The distillation of crude phenol is effected in stills (Fig. 155), holding up to 10 or 15 tons, made of cast or wrought iron and not too high. They are heated from without, with a curtain-arch protecting them against the direct flame. A thermometer is fixed in such a manner that its bulb is at the level of the

[1] For properties, see pp. 209 *et seq.* Much of the following is taken from H. Köhler, *Carbolsäure und Carbolsaurepräparate* (Berlin, 1891).

[2] *Chem. News*, xvi., p. 168.

still-head and the scale is outside. In this first distillation the cooling-worm may be of iron. In distilling, the first fraction consists of everything coming over below 180° ; this is mostly water, with hydrocarbons separating out above and some phenol, which is recovered later on. The second fraction, between 180 and 205°, is allowed to crystallize ; it goes up to the point where a sample of the distillate yields no more crystallizable products. A third fraction is made up to 220°. The residue is either at once run to the creosote oils, or else it is again distilled with a coal-fire or with open steam, in order to yield liquid carbolic acid. In the latter case the last residue is of the nature of soft pitch, and is used as such.

It is of the greatest importance not to work too rapidly, as

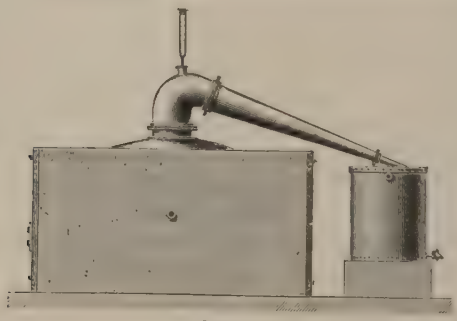


Fig. 155.

the phenol cannot be separated from the cresols if the operation is hastened. Up to the end of the second fraction the distillate should not run in a jet of greater thickness than an ordinary lead-pencil ; afterwards the fire may be increased. The time occupied for a 15-ton still should be from 24 to 28 hours. A skilled workman can manage without a thermometer.

If the distillation is carried on very slowly, it is unnecessary to employ stills with a column-head like that shown in Fig. 156, which, however, is preferred by some manufacturers. Another apparatus, by which phenol is said to be completely separated from its homologues, is shown in Fig. 157. Three or four stills, placed in a row, are simultaneously charged with crude carbolic acid. They are heated by means of coal-fires or by steam-coils ; the first of these must receive superheated steam. The heating

commences in each at the same time; the last stills are stopped when their contents are at 80° C. The heating of the first still is continued, and the vapours given off by it suffice for distilling the contents of the following stills. By this process, it is stated, the last still yields a product crystallizing at once and ready for use.

We can understand the fractionating action of this apparatus, but we doubt whether phenol obtained from it by a rough

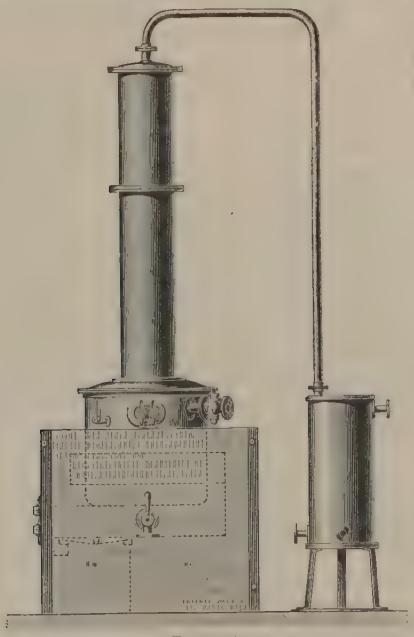


FIG. 156.

distillation will fulfil the present requirements of the trade for crystallized carbolic acid.

According to Marzell,[1] some English manufacturers employ the apparatus constructed by Girard and Delaire for the separation of aniline and toluidine, which must also be suitable for phenols, as their boiling-points very nearly agree with those of the amides. In Fig. 158, *g* represents a still with discharge-

[1] *Chem. News*, xxxviii., p. 105.

pipe (*t*), manhole (*h*), thermometer, vapour delivery-pipe (*a*), and a pipe (*b*) for running back the liquid that comes from the separator (*k*). This separator, formed of lead pipes, is placed in a trough (*i*), filled with pure phenol or with oil or paraffin, heated by a separate fire and covered by a lid in which is fixed a thermometer and a pipe (*d*), which, when phenol is employed, leads to a worm (*r'*) or, in the case of oil or paraffin, into a chimney. The separator itself is connected by *f* with another worm (*r*).

When the still *g* is fired, the vapours pass into *k*, and heat the contents of *i* to the boiling-point of phenol. This is hastened

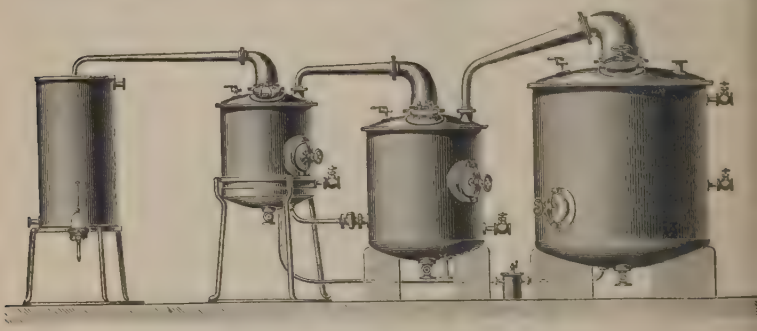


FIG. 157.

by first heating up *i* nearly to that point. The phenol vapour given off in *i* is condensed in the worm *r'*. The vapours passing through the bends of *k* are here separated into a liquid portion, essentially cresol, which collects below in *e* and runs back to *g*, and vapour of pure phenol, which condenses in *r*. When all the phenol has passed over, the cresol, if required, can likewise be obtained pure, *i.e.*, free from less volatile products; but in that case *i* must be filled with oil or paraffin and heated to 201°.

Girard's apparatus might be improved by bending the connecting-pipe *b* so as to make a hydraulic lute, and thus prevent the vapours from passing at once to the back part of *k*. Its action would even then be hardly as perfect as that of the more modern column apparatus, which will be described in the 11th Chapter; and it is indeed quite possible according to

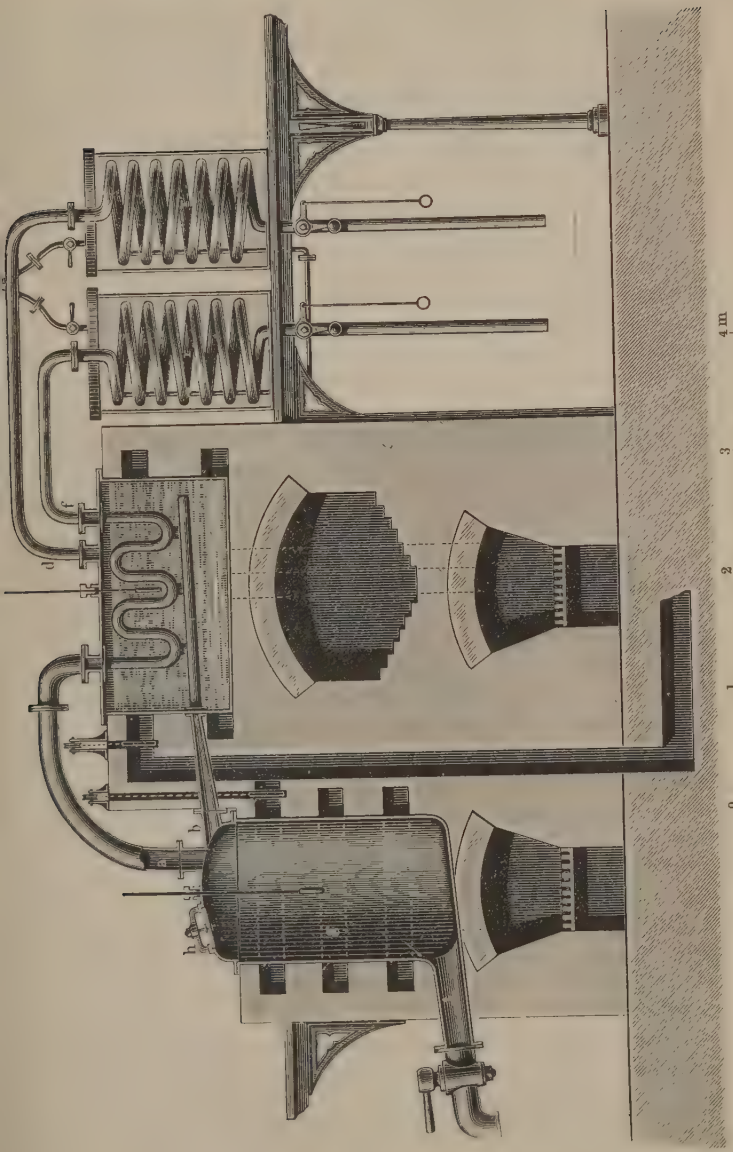


FIG. 158.

private information received from Dr C. Häussermann) to use a Savalle still, such as will be described there, for phenol, with a few slight modifications.

The above-mentioned principal fraction is left to crystallize in a cool place, in large funnel-shaped vessels with a tap below, through which afterwards the mother-liquor can be drained away. The latter is a solution of phenol in cresol and is redistilled. Its separation from the crystals may be facilitated by a centrifugal machine. The above low temperature can be obtained during the summer season sometimes by circulation of cold water, sometimes only by a freezing mixture. At larger works a cooling-cellar is employed. It is best not to go below 12° C., since otherwise the solidifying parts of the product will not come up to the standard.

It is decidedly preferable to charge the crystalling vessels direct from the cooling-room. The first vessels thus yield far more crystals, the cresols accumulating more in the last vessels. These vessels are somewhat deep boxes with handles, made of strong sheet zinc, holding 25 to 40 gallons, which can be loosely suspended in a trough filled with running water. When the crystallization is finished the boxes are placed upside down in a large tray, to draw off the mother-liquor, and the crystals are ultimately further drained in a centrifugal machine with 1500 or 2000 revolutions per minute.

The mother-liquor, and also the third fraction of the first distillate (both separately) are redistilled as described for the first operation, and this is repeated so long as any crystals separate out. It is evident that no general instructions can be given, but that the fractions, which may become very numerous, must be grouped according to their boiling-points, so as to separate the homologues and ultimately cause the boiling-points to become constant within a few degrees, viz., 184° to 188° for carbolic acid and 200° to 203° for cresylic acid. The ordinary crystallized phenol boils at 186°; if the purest, boiling at 182°, is required, the thermometer should be observed accordingly.

For the following detailed description of the manufacture of pure carbolic acid, as practised in Lancashire, I am indebted to Mr Watson Smith:—The crude carbolic acid is distilled in cylindrical wrought-iron stills 2 ft. 9 ins. wide, 2 ft. 2½ ins. high,

with a head $5\frac{3}{4}$ ins. wide, and a thermometer. The worm should be made of zinc—lead, copper, and tin having each been tried and failed. Three different fractions are made; first, water, with some oil; second, good, crystallizable oils; third, oils not crystallizing, containing cresols and napthalene (*cf.* Lowe's prescription, p. 569). If the crude phenol be good, the second fraction will crystallize on standing. It is well agitated with some highly concentrated and pure sulphuric acid, in the proportion of 1 part acid to 50 parts of phenol by weight; with inferior phenol, 2 parts acid to 50 phenol may be used, but never more: and only one such treatment should be employed; otherwise the oils will not crystallize afterwards. In this process the phenol deepens in colour, turns pink, and becomes perceptibly warm. The mixture, well agitated, is poured *at once* (this is very essential) into the still, and distillation commenced and carried through without stopping and starting again. The first products come over between 150° and 160° C.; and the distillate often crystallizes immediately after dropping. Not much comes over below 175°; and it is better to keep this separate. Usually most comes over between 175° and 185°. At this stage the contents of the retort commence to coke, and the process is stopped. The contents of the receiver are let stand for several hours, to cool completely and crystallize. The mass obtained is set to drain for two or three days, the more thoroughly drained upper portions being from time to time removed. To a portion once crystallized no fresh distillate must ever be run, as it would redissolve some of the crystals. Care must be taken not to crush the crystals. The oil that drains from them is technically termed "phenylene." This is again distilled and more crystals obtained from it, which are drained; and the resulting "phenylene" is distilled a third time, but without further treatment with sulphuric acid. In distilling the "phenylene" oils, it is usual to leave in the retort $1\frac{1}{2}$ galls. (sometimes 2) out of every 20, this residue being technically termed "terebene." It is assumed that the latter contains the oils which would prevent the phenol from crystallizing. When the "phenylene" has thus been exhausted by two or three distillations, it is set aside as "bad phenylene."[1]

[1] The terms "phenylene" and "terebene" are used only as private marks, and are not generally employed.—G. L.

In lieu of these repeated fractional distillations it has been found advantageous to artificially cool the "phenylene oil" by refrigerating machines. [That actually employed at the works in question is the ether machine (probably Harrison's or Siebe's; but it is well-known that much better freezing-machines, *e.g.*, Linde's, are in use now.]

All the drained crystals obtained as above mentioned are now fused on a water-bath; the liquid is poured into an iron retort with a zinc worm, and distilled—the first small portion (containing water) being rejected, and most of the remainder received into bottles or other vessels, where it solidifies quickly on cooling, forming a white crystalline mass, which is sold as "pure commercial carbolic acid." The small quantity left in the retort is classed as "terebene oil." A purer product than the above is obtained by placing the bottles upside down for a day, re-fusing the drained mass on a water-bath, and pouring it into fresh, perfectly clean and dry bottles or other vessels. The liquid now sets perfectly hard and very white, and is termed "finished commercial carbolic acid."

For "finished medical carbolic acid" the first crystals obtained from "phenylene oils" by draining all night are melted into a glass retort, and a little of a mixture of equal parts of sodium bicarbonate and pure litharge or red lead, well mixed and pulverized, is added. A very small quantity suffices; the lead oxides probably act in retaining sulphur compounds. After standing for some time, distil into a clean dry vessel, rejecting the portions first coming over, which contain some moisture. The crystals obtained are fused on a water-bath; and the resulting liquid is poured into clean dry bottles, in which, on cooling, it forms pure white and solid crystallized carbolic acid. [The addition of sulphuric acid in the first distillation is not practised anywhere else, and is no doubt the cause of the coking observed at such a low temperature. The dehydration of the phenols is quite easily performed without it. The described process will yield technically pure carbolic acid, but no article suitable for pharmaceutical purposes. Kraemer (priv. comm.) considers the sulphuric-acid treatment, and especially the distillation of the phenol thus, as entirely misplaced, since the distillate will always contain SO_2. He distinctly warns against the method in question.]

The following description of the manufacture of carbolic acid in England comes from an official, and hence authentic, source (*Dr Ballard's Sanitary Report to the Local Government Board*, for 1878, p. 151). Carbolic and cresylic acids are prepared from the crude acids by a series of fractional distillations and crystallizations. For these distillations iron stills, capable of dealing with charges varying from 150 to 500 gallons, are used; they are heated by a fire beneath. The crude acid is transferred from the casks in which it arrives at the works to a closed tank, preferably sunk in the ground, from which it is pumped into the still. The residue of the first distillation, which is or ought to be conducted to dryness, is a light and spongy coke, which, when the still is cool, is broken up with an iron bar and removed through the manhole. It is used as fuel. During the last part of this first distillation offensive uncondensable gases are given off. When, on subsequent distillation, an acid is distilled off which solidifies at a higher temperature than that which results from the first distillation, the acid is apt to solidify in the pipe, and hence the pipe leading to the condenser is provided in its course with a short-necked opening, capable of closure, through which, if necessary, hot water may be introduced to clear the pipe. The products of condensation are collected in numerous small fractions, and are usually received in a series of galvanized iron vessels, which are left open during the process of their filtering, but covered with a lid when they have become full. Carbolic acid is most abundant in the earlier, and cresylic acid in the latter, fractions. The vessels containing the products of distillation are then set aside to cool, when the carbolic acid crystallizes, while the cresylic acid, holding some carbolic in solution, remains liquid. The liquid matter is then drained off through an opening near the bottom of the vessel, and is subjected to a second distillation for the purpose of obtaining the carbolic acid it contains. When all the liquid has been drained off from the crystals, or removed by the aid of a centrifugal machine, the carbolic acid obtained is again distilled, and the cresylic acid, after crystallization of the carbolic acid in the receiving vessels, is drained off by inverting the latter over a trough. By the first distillation and crystallization, as conducted at Lowe's works, a carbolic acid fusing at 29°·5 C. is obtained. The second distillation and

crystallization gives an acid fusing at 35° C. The acids, of the fusing-points mentioned above, are next melted in a steam-jacketed vessel and mixed with water; the liquid hydrate of cresylic acid is separated mechanically in the usual manner; and the solid crystalline hydrate of carbolic acid is submitted to fractional distillation, by which process the fusing-point of the dry acid is raised to 42°·2 C. All these are "commercial" acids, and for medical purposes still require refining, in order to remove from them the last traces of neutral hydrocarbons, of the offensive sulphuretted compounds, tar-bases, etc. At Calvert & Co.'s works the commercial acids are refined by suitable acid treatment for the removal of the bases and neutral hydrocarbons, and by treatment with acetate of lead for the removal of sulphuretted hydrogen. After this the acid is re-distilled in glass retorts heated by a sand-bath, each retort taking a charge of about 40 lb., of which four-fifths are distilled off. The residue in the retorts is a blackish, treacly substance which crystallizes imperfectly, and which is dealt with elsewhere for the recovery of such carbolic acid as it contains. The liquid cresylic acid which results from earlier operations is refined in a similar manner by distillation with acetate of lead; but an iron still is used for this process, and the distillation is carried to the production of a coke.

In order to prevent the *nuisance* arising from the escape of offensive uncondensable gases, which are sometimes perceptible for a distance of at least 100 yards, the following arrangement is carried out at Mr Lowe's works. The pipe from the worm condenser, at a distance of a few inches from the place where it issues from the tub, divides into two branches, one of which descends and carries off the condensed liquid, a gas-trap being formed by a bend of the pipe. The other branch ascends and conducts any uncondensed gases to a 6-inch main pipe, which runs along the front of the whole range of stills. From this main a pipe conveys the gases to a small worm condenser, and from this to a stoneware bottle which receives all liquid matters condensed here. A pipe proceeding from this bottle is supplied with a steam-jet, which aspirates the gases from the main and drives them onwards through water or milk of lime, contained in a cask, whereby sulphuretted hydrogen is arrested; and from this washer a pipe conveys the residual gases into the

ash-pit of a fire. Should the gases chance to ignite, the ignition would not proceed further back than the cask.

The open receivers, described above, are a source of nuisance, from the general odour of crude carbolic acid. This may be considerably lessened by receiving the condensed liquids into covered vessels, as shown in Figs. 159 and 160. A series of deep narrow pans (*a a*) are set side by side, with intervals of a few inches between them, within a wooden case (*b*), filled with brine, which can thus circulate around and between

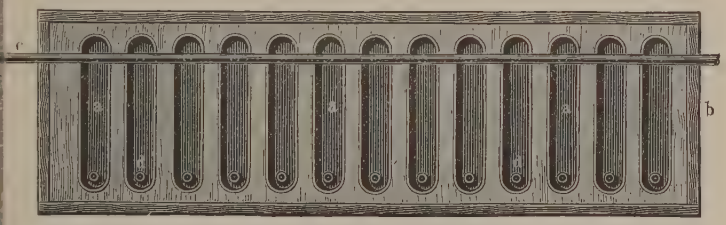


FIG. 159.

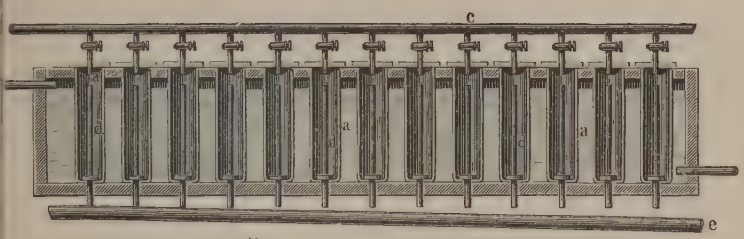


FIG. 160.

the pans. All the upper part of the case is closely covered, so that only the tops of the receivers are seen, which are kept covered by wooden covers. The condensed products are conveyed by a pipe (*c*), having small branch pipes with taps opposite the several receiving-pans, which pipes discharge into the pans below their covers. Should any pan become too full, the surplus can be run off from the upper part by a waste-pipe (*d*), screwed into the bottom of the pan, into a drain or channel (*e*) beneath, leading to the liquid acid tank. The brine which circulates round the pans is cooled by means of a freezing-machine. The crystallization of the acid thus takes place more

speedily and completely; when it is finished, the pans are uncovered, the pipes *d d* are removed, and the liquid portion then runs off into the drain *e*.

Riehm[1] has described a process for separating phenol and cresols by means of their barium salts, which we shall refer to in detail when treating of the purification of the cresols.

Absolutely Pure Carbolic Acid.—By the methods hitherto described it is possible to obtain crystallized carbolic acid, but hardly an article remaining white, fusing at 42° and boiling at 182°. On the contrary, the maximum fusing-point thus to be reached is 38°, and on standing for some time the acid turns red, partly liquefying, the liquid portion being discoloured. The lower melting-point is not caused by the presence of water, but by para- and orthocresols, which cannot be removed by fractionation, as the boiling-points differ too little (phenol 182°, orthocresol 185° or 186°). But a separation can be founded on the fact that carbolic acid forms with water a crystallizable hydrate, whilst the cresols yield liquid hydrates.

This observation was first made in 1862 by Lowe, who thereupon founded the manufacture of purest carbolic acid.[2] He added to fused crystallized carbolic acid a certain quantity of water, and cooled down to 4° C.; thus he obtained a phenol hydrate, $C_6H_6O + H_2O$, crystallising in large octahedra, from which the mother-liquor, containing all the cresols, could be separated by draining and centrifuging. The hydrate on distillation yielded first water, and then phenol, fusing at 41 and boiling at 182°.

Some more details are given in Lowe and Gill's patent.[3] To ordinary phenol, according to whether it crystallizes at 16·5 or 35 C., from 5 to 30 per cent. water is added, with heating and agitating, the solution being afterwards cooled down to −9°·5 or +10°, and the crystals treated as above. The product may be obtained absolutely pure by repeating his treatment.

Crace Calvert (*loc. cit.*) believed the composition of the hydrate to be $(C_6H_6O)_2H_2O$, but Alexejew[4] could not obtain this.

Church[5] purifies phenol by precipitating it from its aqueous

[1] Ger. P. 53307.
[2] Crace Calvert, *Chem. News*, 1867, pp. 57, 297, 310, 320.
[3] *Cf.* Marzell, *Chem. News*, xxxvii., p. 105.
[4] *Chem. Centr.*, 1881, p. 51. [5] *Chem. News*, xxiv., p. 173.

solution by common salt and distilling over quicklime. This is impracticable, on account of the great loss of carbolic acid.

The process now universally employed for the preparation of absolutely pure phenol is substantially that of Lowe and Gill, and is carried out on the large scale as follows:—Crystallized carbolic acid, purified by distillation in the ordinary manner, is once more distilled, this time in an oil-bath, in a still holding at most 20 cwts. and working very slowly. The first runnings contain a little water; the principal fraction is carbolic acid, fusing at 30° or 32°, and the distillate is turned into another receiver when the fusing-point falls below 25°. This last product is combined with the corresponding portions of the first distillations. The principal, purer fraction is fused in enamelled iron pans in the water-bath, stirred with 5 or 10 per cent. distilled water and allowed to cool. The phenol hydrate separating out is drained, centrifugalled, and again distilled in an oil-bath. This time the still must be provided with an enamelled or (preferably) silver head. The cooling-worm must not be made of iron; if the still-head is long enough, the worm may be made of stoneware, but the connection between them must be below the level of the cooling-water, to prevent cracking of the stoneware. Since the price of silver has gone down very much, it is also used for the worms. Iron enamelled inside has not turned out practicable; aluminium (recommended by Donath, *Z. angew. Chem.*, 1895, p. 141) is entirely excluded, since Zmerzlikar (*ibid.*, 1895, p. 468) noticed that it is strongly attacked by carbolic acid.

The first distillate consists of an aqueous 5 per cent. solution of carbolic acid (saleable as such) and a lower layer of pure carbolic acid, liquid on account of containing some water, which is put back into the still for the next operation. The second fraction is pure carbolic acid, fusing at 41° or 42°, which is at once put into the (properly cleaned) tins or glass bottles in which it is to be sent out for sale. The small residue in the still is worked up again in the first distillation.

Carbolic acid in the pure state is also produced *synthetically* from benzene, by the reaction of Wurtz, Kekulé, and Dusart:

(1) $C_6H_6 + SO_4H_2 = H_2O + C_6H_5(SO_3H)$;
(2) $C_6H_5(SO_3K) + KOH = C_6H_5 \cdot OH + K_2SO_3$.

This process formerly could not be considered as commercially practicable, but the British Consul at Stuttgart reports officially in 1902 that the prohibition of the exportation of carbolic acid from Great Britain in January 1900 had caused the German manufacturers to produce carbolic acid by synthesis (*Chem. Zeit.*, 1903, p. 229).

The Reddening of Carbolic Acid.

The reddening of carbolic acid under the influence of light and other agencies has been the subject of many investigations, but is even now not clearly understood. Hager[1] attributes it to ammonia or ammonium nitrite, taken up from the air; Yvon[2] to rosolic acid; several other authors to the presence of metallic compounds, *e.g.*, Sicha[3] to copper, Meyke[4] to lead, Fahlleusch[5] to iron; Kreusel[6] believes that copper has the greatest influence, silver, lead or zinc less, tin none. The colouring principle is soluble in sulphuric acid with blue colour, whilst rosolic acid yields a yellow solution. Mylius[7] comes back to ammonia, and recommends counteracting its influence by a slight addition of hydrochloric acid; but this certainly does not help in all cases. Kraemer[8] accuses certain aldehydes, Spilker[9] indene, Bidet[10] thiophenes (this is one of the most likely explanations). Schneider[11] found that synthetic carbolic acid reddens as well as that prepared from tar. Fabini[12] found that the colouring substance can be prepared in considerable quantities by the action of cupric sulphate upon ammonium phenylate. It is a black, resinoid substance, which he calls "phenythren," which on heating forms a yellow vapour and sublimes in the shape of a pink body soluble in concentrated sulphuric acid with blue colour. It leaves no ashes and therefore contains no metal; the metals active in its formation play only an intermediate part by forming metallic phenylates,

[1] *Pharm. Centr.*, 1880, p. 77; 1883, p. 447.
[2] *Pharm. Journ. and Transact.*, 1882, p. 1051.
[3] *Chem. Centr.*, 1892, p. 486.
[4] *Pharm. Zeitsch. f. Russland*, xxii., p. 427.
[5] *Pharm. Centr.*, 1885, p. 6.
[6] *Chem. Ind.*, 1886, p. 84.
[7] *Pharm. Centr.*, 1887, p. 72.
[8] *J. Gasbeleucht.*, 1887, p. 879.
[9] *Berl. Ber.*, 1896, p. 561.
[10] *Monit. Scient.*, 1889, p. 487.
[11] *Pharm. Centr.*, 1890, p. 68.
[12] *Chem. Ind.*, 1892, p. 118.

decomposed by hydrogen peroxide into colouring-matter and metal. 0·004 g. suffices to impart a slight pink shade to 1 kg. of carbolic acid; 0·1 g. gives a dark red colour.

Kohn and Fryer[1] in an extensive investigation found that the chemically pure ("absolute") phenol of commerce, specially purified by 15 redistillations, showed the same reactions as synthetic phenol and that made from the salicylic acid of wintergreen oil. All of these phenols were coloured by pure hydrogen peroxide without the presence of metallic compounds, but the latter hastened the reaction. Concentrated ammonia imparts a blue colour; dilute ammonia, caustic potash, hydrogen peroxide, a pink colour; the light has only a quickening action. Thoroughly dry air does not act upon phenol, nor does water in the absence of air; but moisture in the presence of air reddens phenol even in the dark, and more quickly in the light.

Richardson,[2] on repeating Kohn and Fryer's experiments, found that under all circumstances hydrogen peroxide is formed when phenol meets with moist air, and that this is the reddening agent. Like Kohn, he found that behind dark red glass no reddening took place, but no H_2O_2 was formed in this case.

Hankó[3] declares the reddening of phenol to be due to an oxidation, promoted by the presence of metals (especially copper) and ammonium compounds, and preventable by introducing tin protochloride (also by keeping in tinned iron). The colouring-matter is less volatile than carbolic acid, and remains behind in distillation; it is *not* corallin, and it stains carbolic acid even in the proportion of 1 : 200,000.

The reddening, according to Gordon, is caused by ozone or hydrogen peroxide, present in the air. Boes (*Pharm. Zeit.*, 1902, p. 448) explained it by the presence of the "isophenols," indicated by Brunner, but this will hardly hold good, since Brunner himself later on found that his "isophenols" did not exist (*Chem. Zeit.*, 1902, p. 1123).

According to Ebell,[4] crystallized crude carbolic acid contains substances which are volatile and colourless, but are changed into non-volatile, red or yellowish-brown substances by the action of light, more than by that of heat and air. The substance yielding the red colour passes over principally along

[1] *J. Soc. Chem. Ind.*, 1893, p. 197. [2] *Ibid.*, 1893, p. 415.
[3] *Fischer's Jahresber.*, 1892, p. 447. [4] *Rep. f. anal. Chemie*, 1884, p. 17.

with the first, that yielding the yellow colour with the last products of distillation. Neither of them in partial crystallization enters into the crystals of carbolic acid, apart from what is mechanically enclosed in them, but remains in the mother-liquid. They are sparingly soluble in water, but are extracted by water acidulated with sulphuric or phosphoric acid; they are insoluble in benzene. Oxidizing agents, acting during the distillation, change the substance yielding the red colour more than that yielding the yellow colour; oxidizing agents in aqueous solution and in the presence of sulphuric acid destroy them both. The products of oxidation seem to be less soluble in water than the original substances; they are not volatile, or pass over only with the highest boiling fractions. Even the acids distilled from glass vessels often colour very strongly; in such acids no traces of metals could be found.—It is recommended to purify the crude acid by repeated crystallization and subsequent distillation of the crystals. If it is not possible to work up the red mother-liquors, or to sell them at a fair price as "100-per-cent. liquid carbolic acid," it is recommended to treat them with an oxidizing agent in the presence of sulphuric acid, and to follow this up by repeated washings. In less difficult cases it is sufficient to add to the contents of the retort, previous to distillation, a little red oxide of lead with a small admixture of sodium bicarbonate, or some finely pulverized barium peroxide.

A special treatment for *preventing this reddening* of otherwise pure carbolic acid is only exceptionally necessary if the solution of sodium phenate is properly purified and the fractionations are well performed, but we shall enumerate the proposals made in that direction.

We first mention the process of H. Müller,[1] who at the same time introduces fractional precipitation (analogous to the fractional saturation mentioned by Behrens, p. 568) of the crude carbolic acid before distillation. The alkaline carbolic liquid contains, besides carbolic acid, some oxidizable bodies which give rise to a brown coloration, and also, especially in concentrated solutions, a considerable quantity of naphthalene and other indifferent substances insoluble in water by themselves. It is diluted with water till further addition ceases to

[1] *Dingl. polyt. J.*, clxxix., p. 461.

precipitate naphthalene;[1] the dark brown liquid is exposed to the air in a shallow vessel for several days, with frequent stirring; it is then filtered, its percentage of phenols ascertained, and the quantity of sulphuric acid necessary for precipitating the whole of them calculated. If now only $\frac{1}{6}$ or $\frac{1}{8}$ of the calculated acid is added with frequent stirring, at first the resinous substance, changed by the action of the air, is precipitated, mixed with more or less of the phenols. A further addition of acid precipitates essentially cresol; and after a few trials almost pure phenol, crystallizing after a single distillation, can be obtained by the third and last precipitation. In order to remove the water, a current of dry air is passed over the phenol heated almost to boiling. The aqueous vapour is usually accompanied by an unpleasantly smelling substance, according to Müller a sulpho-compound of phenol, which can be removed by adding a little lead oxide before distilling. (Such sulphur compounds no doubt exist already in the tar; but they may also be formed afterwards by incautious precipitation with strong sulphuric acid, as pointed out, p. 578.)

The exposure of the liquor in shallow pans with frequent stirring, recommended by Müller, would no doubt be advantageously replaced by forcing in a finely divided current of air, or by running the liquor down a coke column, etc. The same object is attained[2] by adding $\frac{1}{5}$ or $\frac{1}{3}$ per cent. potassium bichromate, and the sulphuric acid necessary for decomposing this, to the crude carbolic acid in the still, and heating gently at first. If this does not suffice to make the phenols distil colourless, more bichromate must be added.

It has been recommended[3] to treat crude (50-per-cent.) carbolic acid with 1 per cent. of potassium bichromate and the corresponding quantity of strong sulphuric acid in a shallow pan, running in first the acid, then the solution of bichromate, and agitating the mixture for several hours with access of air and in a place exposed to the direct light of the sun. The mixture is allowed to settle, the oil is drawn off and distilled, and the fraction coming over between 170° to 198° is again

[1] This stage of the dilution is not very easily detected; hence it is preferable to employ dilute alkali from the first, as already pointed out.

[2] Stohmann-Kerl's *Chemie*, vi., p. 1182.

[3] *Fischer's Jahresber.*, 1885, p. 465.

submitted to the bichromate treatment, and is redistilled in a still with rectifying-column.

Reuter (*Chem. Centr.*, 1905, i., p. 1012) contends that the reddening of phenols can be prevented by the use of a small quantity of sulphurous acid, and redistilling in a current of CO_2, to exclude air. He recommends that the pharmacopœias should directly prescribe the colour of carbolic acid to be red!

P. W. Hofmann has obtained a patent (Ger. P. 67696) for preventing the discolouring of phenol by precipitating the impurities by a solution of stannous chloride.

Walter,[1] who attributes the reddening to the presence of iron in the glass bottles, recommends coating the glass inside with paraffin.

Demant[2] liquefies red carbolic acid in a water-bath, with addition of 10 per cent. spirit of wine, and cools down. When most of the liquid has solidified, the mother-liquor is drained off; the crystals are then again obtained in a white state.

From the above we may conclude that, in the manufacture of carbolic acid, it is no use trying to prevent the reddening under any circumstances. Good drying and keeping away metallic contaminations will delay, but not entirely prevent, the reddening, nor will this be done by the addition of oxidizing agents in the distillation, since the purest phenol reddens in the presence of air and moisture. But it is certain that the red colouring-matter is entirely harmless for medicinal uses.

Marzell (*Chem. News*, xxxvii., p. 105) recommends an addition of alkaline plumbate solution for decomposing the *nauseous sulphur compounds*. This is probably better than Müller's plumbic oxide, or than the addition of red lead and sodium bicarbonate, as practised in Lancashire according to Watson Smith. Casthelaz employs a solution of sodium bisulphite for a similar purpose.

Sharpe's paper on the manufacture, purification, and application of carbolic acid (*J. Soc. Dyers and Col.*, 1884, p. 146) can only be mentioned here.

Commercial Cresols.

A large quantity of products, consisting essentially of a mixture of the three isomeric cresols with a little phenol and

[1] *Chem. Zeit.*, 1899, p. 47. [2] *Ibid.*, 1887, p. 78.

xylenols, is produced especially by the German tar-works, as a by-product from the manufacture of pure carbolic acid, obtained by fractionation of the crude carbolic acid.

These products are sold by the name of *Rohkresol* (crude cresol), "crude carbolic acid 50 per cent." and "crude carbolic acid 25 per cent." A special investigation of these products has been made at the German Board of Health, by Carl Fischer and P. Koske, and is published in the *Arb. d. Kais. Ges. Amts.*, xix., p. 577-671, abridged in *Chem. Centr.*, 1903, i., 384-5. We shall quote the most salient points of that work.

Rohkresol consisted of:—

0·35	per cent.	water.
2·34	„	phenols, boiling up to 188° (a mixture of phenol and cresols).
94·5	„	mixture of the three isomeric cresols, boiling from 188° to 202°.
1·23	„	mixture of cresols with a little xylenols, „ 202° „ 210°.
0·06	„	higher phenols „ „ „ 210° „ 225°.
0·07	„	residue.

Traces of pyridine bases.

"Crude carbolic acid 50 per cent." showed in 100 phenols: 27·6 per cent. cresols, 54·10 per cent. mixture of cresols and xylenols, 10·90 per cent. highest boiling phenols; first runnings, etc., 7·40 per cent.

"Crude carbolic acid 25 per cent." showed in 100 phenols: 4·02 first runnings, 22·66 cresols, 43·60 mixture of cresols and xylenols, 6·90 xylenols, 3·94 phenols boiling from 220° to 270°, 17·98 phenols boiling over 270°. Besides the phenols (25 per cent.) there were 75 per cent. non-phenolic substances. The authors tested these products, as well as a number of other commercial carbolic-acid preparations, for their bacteriological action, but into this we cannot enter here.

Liquid Carbolic Acid, water-white, consists of the redistilled mother-liquors from crystallized carbolic acid, containing the three cresols (sold by the firm of Schering as "*tricresol*"). Hammerl (*Z. angew. Chem.*, 1897, p. 569) states that its bactericidal properties are twice as strong as those of a solution of carbolic acid of equal percentage. The fault of slight solubility has been remedied by the preparation of "*lysol*" and "*creoline*" (pp. 527 and 565).

The Preparation of Pure Cresols.

The mother-liquor remaining after completely exhausting all the crystallizable carbolic acid, contains but little carbolic acid, together with all the cresols. It forms a limpid liquid of 182 to 200° boiling-point, and of a disagreeable smell, quite different from carbolic acid. The boiling-points of the isomers do not differ very much :—

Orthocresol	191°.
Metacresol	203°.
Paracresol	202°.

Hence their separation by fractionation is not possible, all the less as their relative proportions are not always the same. Both Ihle[1] and Tieman and Schulze[2] found mostly ortho- and paracresol, with little metacresol; but K. E. Schulze[3] obtained about 40 per cent. meta-, 35 per cent. ortho-, and 25 per cent. paracresol in tar oils. Gruber[4] found that water of ordinary temperature dissolves 2·5 per cent. (by volume) of pure ortho-, 0·53 per cent. of pure meta-, 1·80 per cent. of pure paracresol, 2·20 per cent. of the mixture prepared from toluidine, 2·55 per cent. of that prepared from tar oil.

Nördlinger[5] establishes the following properties of tar-coal cresol :—Water dissolves 2 to 3 per cent., and is itself soluble in cresol in the proportion of 15 or 20 to 100 cresol. Cresols are easily soluble in animal, vegetable, and tar oils, less so in "mineral oils." They dissolve 20 to 30 per cent. of mineral oils. The reciprocal solubility of cresol and oils increases with the percentage of oils, and decreases with that of water. Anhydrous concentrated oily solutions of cresol attract water, and are ultimately separated into two layers, one of aqueous cresol and the other of oil floating above. Much water is able to extract cresol from its solution in oil, but by shaking with oil cresol can also be extracted from aqueous solutions.

The *poisonous and antiseptic properties* of the three cresols, according to Gibbs and Hare (*Arch. d. Physiol.*, 1889, p. 289) are different. The lethal doses for 1 g. of nervous substance of the frog is 0·004 ortho-, 0·006 para-, and 0·044 metacresol. Quite a

[1] *J. prakt. Chem.* [2], xiv., p. 451.
[2] *Berl. Ber.*, xi., p 768.
[3] *Ibid.*, xx., p. 410.
[4] *Fischer's Jahresber.*, 1893, p. 539.
[5] *Z. angew. Chem.*, 1894, p. 166.

number of communications have been made on this point in 1906 and 1907, and are reported upon in *Chem. Centr.*, 1906, ii., pp. 1510, 2070; 1907, i., p. 835; ii., pp. 85, 2070.

J. Herzog (*Apoth. Zeit.*, 1907, p. 78; *Chem. Zeit. Rep.*, 1907, p. 73) makes the following statements: *o*-cresol (b.-p. 190°·8) has least action; *p*-cresol (201°·8) is most poisonous; *m*-cresol (202°·8) the most efficient antiseptic.

Rapp (*Chem. Centr.*, 1907, ii., p. 717) on the contrary finds that *o*-cresol is at least equal in bactericidal action to *p*-cresol, and almost as much so as *m*-cresol.

The medical cresol should be a yellow or brownish liquid of neutral reaction, easily soluble in alcohol and ether, clearly soluble in 100 parts of cold water, boiling at 198° to 202° C. With this crude cresol and a linseed-oil soap (containing 70 per cent. fatty acid) a solution of cresolic soap is obtained, equal in disinfecting power to lysol.

These properties are important in connection with the application of the cresols for disinfecting purposes, for which, according to several authors, the tar cresols are much more efficient than pure carbolic acid; in solutions of the same percentage, Hammer[1] found the former from four to ten times as efficient as the latter, and similar results have been published by Deplanque,[2] Gruber,[3] and Seybold.[4]

Separation of the Three Isomeric Cresols.

Quite a number of processes has been worked out for this object, since the single cresols are required for preparing colouring matters, etc.

Riehm (Ger. P. 53307, *Z. angew. Chem.*, 1890, p. 647) utilizes the various solubilities of barium phenate and cresylates in water. (The patent has been allowed to lapse.)

Lederer (Ger. P. 79514, *Z. angew. Chem.*, 1895, p. 114) bases his process on the various solubilities of cresoxacetic acids in benzene and the sodium cresoxacetates in water.

Byk (Ger. P. 100418) effects the separation by means of molecular compounds of the phenols with calcium chloride,

[1] *Arch. f. Hyg.*, xii., p. 359.
[2] *Bull. therap. d. Arch. de Pharm.*, 1888, p. 453.
[3] *Jahresber. Fortschr. Pharmakogn.*, 1893, p. 389.
[4] *Chem. Zeit.*, 1899, p. 35.

and many other inorganic and organic salts ("crystal-phenols"). This patent lapsed already in 1901.

Rud. Rütgers (Ger. P. 137584; B. P. 286, of 1902) introduces anhydrous oxalic acid into the crude mixture of cresols, previously freed from phenols while heating the mixture. Thus the oxalic ester of paracresol is formed, which separates out on cooling and is decomposed by water. Ortho- and meta-cresol are afterwards separated by fractionating. This patent as well as an additional one (Ger. P. 141421), in which, in lieu of oxalic acid, oxalates were recommended, lapsed in 1905.

Vidal (Fr. P. 315695, of 1901) treats the crude cresols with the sulphate of zinc, calcium or aluminium, and a nitrate, whereby an insoluble metallic nitroso-derivate of paracresol is formed.

The Chem. Fabr. Ladenburg (Ger. P. 148703; B. P. of Schulze & Ladenburg, 1881, 1904) separate *m*- and *p*-cresol by sulphonating them at a temperature of 110° C. with sodium bisulphate containing sodium pyrosulphate. This transforms *m*-cresol into its sodium sulphonate, while the *p*-cresol is not acted upon. The same inventors (Ger. P. 152652) also prepare a crude (71 per cent.) *m*-cresol from the mixture of calcium cresolates, formed by milk-of-lime; the neutral calcium *m*-cresolate, being very little soluble, is precipitated and is separated from the solution containing most of the *p*-cresol (*Chem. Centr.*, 1904, ii., p. 168).

Kalle & Co. obtained in 1894 a German patent for the manufacture of synthetic metacresol which lapsed in 1903, evidently because that substance is now isolated more cheaply from coal-tar creosote. Also Hauff & Co. (*Chem. Zeit.*, 1899, Rep., p. 35).

The Farbenfabriken vorm. Bayer & Co. (B. P. 9953, of 1904), in order to separate mixtures of *o*- and *p*-cresols, add to these a suitable quantity of KOH, and heat the mixture till solution has taken place. The crystals of the *p*-compound, which deposit on cooling, are separated by filtration, washed with alcohol and treated with hydrochloric acid to separate the *p*-cresol. The filtrate from those crystals is also treated with hydrochloric acid to obtain *o*-cresols.

Raschig (Ger. P. 112545), after having removed most of the *o*-cresol by fractional distillation, separates *p*- and *m*-cresol by sulphonating the mixture. On diluting and cooling, the *p*-cresol-sulphonic acid crystallizes out as such, or in the shape of

its sodium salt. The sulphonic acids are decomposed by superheated steam, and yield the pure cresols. Or else (Ger. P. 114975) the sulphonated mixture is at once treated by superheated steam at a certain temperature, whereby only metacresol is split off and distils over, after which the paracresol-sulphonic acid is split up in the same manner at a higher temperature.

Raschig[1] has worked out another process for separating *m*-cresol from *p*-cresol (Ger. Ps. 144903 and 146752). Commercial cresol on an average contains 40 per cent. *o*-cresol, 35 *m*-cresol, and 25 *p*-cresol. When treated with nitric acid, the *o*- and *p*-cresol are destroyed, and 60 parts of pure trinitro-*p*-cresol are obtained. To avoid the great loss of nitric acid in this operation, at least partially, it is expedient to separate by a number of careful fractional distillations the *o*-cresol, boiling at 188° C. Since both *m*-cresol and *p*-cresol have the same boiling-point, 199°·5 to 200°, they cannot be separated by fractionation, but the mixture of 60 per cent. *m*-cresol and 40 per cent. *p*-cresol presents already a great advantage over the first material, as it yields a 100 parts of trinitro-*m*-cresol, and wastes less nitric acid. That mixture now forms an article of trade, and in it the percentage of *m*-cresol can be estimated by a process which will be described later on.

Yield of pure products from Crude Carbolic Acid.

In Muspratt-Stohmann's *Chemie*, 3rd ed., vol. vi., 1884, this is stated as follows :—

Sources of the tar.	Nature of the starting material subjected to the alkaline treatment.	Pure product boiling between 188° and 208°.	Crystallized carbolic acid obtained therefrom.	Liquid carbolic and cresylic acids.
		Per cent.	Per cent.	Per cent.
South Germany . .	Light oil.	34·7	13·1	21·6
Do. . .	Creosote oil.	44·8	...	44·8
Saxony . . .	Light oil.	33·1	13·9	19·2
Saxony, Rhineland, Vienna . . .	?	30·4	6·0	24·4
Sundry . . .	Light oil.	43·7	29·8	13·9
South Germany and Saxony . .	Light oil.	41·0	28·0	13·0

[1] *Z. angew. Chem.*, 1900, 759.

The considerable loss which takes place in the working-up of crude carbolic acid is caused by its percentage of empyreumatic products, neutral hydrocarbons (especially naphthalene), tar-acids boiling above 203°, and working-losses.

According to Wurtz,[1] sundry tars contain the following quantities of "phenol" [which probably means all "tar-acids"]:—

Tar from Wigan cannel coal . .	14 per cent.
„ Staffordshire coal . .	9 „
„ Newcastle coal . . .	5 „
„ Boghead	5 „
„ certain kinds of peat . .	15 to 20 per cent.

The German tars yield on an average 5 or 6 per cent. of phenols, of which about one-third are crystallized carbolic acid.

Watson Smith gives the following analysis (by Lowe's method, see p. 608) of crude carbolic acid from Manchester and Blackburn tar, both made from Wigan cannel coal:—

	Blackburn.	Manchester.	Manchester.
	Per cent.	Per cent.	Per cent.
Water (per cent. by volume) . . .	12	13	15
First oil, boiling up to 185° (to be thrown away)	11	11	10
Carbolic acid distilling below 190° . .	48	45	45
„ „ „ 195° to 196° .	13½	17½	17½
Solidifying-point of these = 61½ to 62½ per cent.	15°	18°	16¾°

One thousand galls. of carbolic oil from Manchester tar yield about 50 galls. crude carbolic acid.

Rütgers[2] states the yield obtained at his own works from coal-tar = 0·2 per cent. crystallized carbolic acid, and 0·3 per cent. liquid cresol.

South German tars, according to Stohmann (*loc. cit.*), yield 0·33 per cent. crystallized carbolic acid, 0·48 per cent. liquid carbolic acid (with a little cresol), 3·20 cresols (with a little phenol). Köhler[3] obtained from South German tars 0·3 crystallized carbolic acid (38 fus.-pt.) and 0·5 cresols; Kraemer,[4] from North German tars, 0·35 to 0·50 per cent. phenol, and 0·60 to 1·20 per cent. cresols.

[1] *Dictionnaire de Chimie*, ii., p. 820.
[2] *Chem. Ind.*, 1879, p. 282.
[3] *Carbolsaüre*, etc., p. 97.
[4] *J. Gasbeleucht.*, 1887.

Most of these statements do not take any account of the phenols in creosote oil. The yield of phenols from coal-tar has been mentioned also in the general statements, pp. 409 *et seq.*, and that from blast-furnace and coke-tar, pp. 113 *et seq.*, and 137.

Analysis of Carbolic Acid.

Carbolic acid occurs in commerce in different qualities—as crude carbolic acid, often with the indication of a certain percentage of phenol, as crystallized carbolic acid of different degrees of purity, and as liquid carbolic acid. The latter contains mostly the higher homologues, cresol (cresylic acid), phlorol, etc.; but sometimes there is sold, for medical purposes, "liquefied pure carbolic acid" (acidum carbolicum liquifactum), consisting of 90 parts pure phenol and 10 parts water or alcohol.

Testing of Crude Carbolic Acid.

The properties of crude carbolic acid have been mentioned, p. 583.

C. Arnold and G. Werner (*Apoth. Zeit.*, 1905, p. 925; *Chem. Zeit. Rep.*, 1905, p. 381) give the following reactions for *distinguishing phenol and cresols.* Mix 10 c.c. of the aqueous solution, with caustic soda solution, alcohol, and 1 drop aniline. Shake up, add 5 or 6 drops hydrogen peroxide, shake again, and add 12 drops of a solution of sodium hypochlorite. The colour reactions are then as follows:—Phenol yields red colour, passing over into yellow; ortho- and metacresols violet, at once changing into green; para-cresol purple red, quickly vanishing. The latter is disinguished from phenol and the other cresols in this way. Dissolve 2 drops (if necessary, after liquefying) in 3 c.c. concentrated sulphuric acid and add a trace of potassium nitrite, then *p*-cresol yields a dark red, phenols *o*-, and *m*-cresol and tri-cresol an emerald green colour. With ferric chloride *o*-cresol yields a blue colour rapidly turning green; *m*-cresol and phenol, purple; *p*-cresol, blue.

The percentage of phenols in crude carbolic acid can be *approximately* tested by shaking it up in a graduated tube with twice its bulk of 9 per cent. caustic-soda solution, added

gradually. This is the usual process; that of Hager[1] (employment of an alcoholic solution of potash) is less used. The volume of the neutral oils (which may be at the top or at the bottom) is now read off. The separation of the oily and aqueous layers) becomes more accurate if (as first proposed, by Hager) a quantity of petroleum spirit is added in equal volume to that of the tar oil; of course this volume must be deducted. This or any similar test cannot possibly be accurate, because the alkaline solution, especially if it be somewhat concentrated, dissolves indifferent oils and naphthalene. A check upon the reading of the volume of the neutral oils is: saturating, in a graduated tube, a measured portion of the alkaline liquor with hydrochloric acid and reading off the volume of the phenols separated. Beckurts[2] estimates that the phenols will dissolve about as much water as the water will dissolve phenols, and even prefers, for *crude* carbolic acid, this test to Koppeschaar's (see below).

The following prescription for testing crude carbolic acid was drawn up by Mr Charles Lowe, in the first instance as an instruction to those tar-distillers who supplied him with their products, and is followed at most English and some continental works. The sp. gr. should be between 1·055 and 1·070. One thousand fluid grains (or, say, 200 c.c.) of the oil are distilled in a retort, without any special condensing-apparatus, and the liquid passing over is collected in graduated tubes. Water first distils, and is followed by an oily fluid. When 100 fluid grains of the latter have been collected, the receiver is changed. The volume of the water is then read off. If the oily liquid floats on the water, it contains light tar oil. It should be heavier than water, in which case it may be regarded as hydrated acid containing about 50 per cent. of real carbolic acid. The next portion of the distillate consists of anhydrous acid; and when it measures 625 g. the receiver is again changed. The residue in the retort consists wholly of cresylic acid and still higher homologues of carbolic acid. The 625 grains measure of anhydrous carbolic acid contains variable proportions of carbolic and cresylic acids. These may be approximately determined by ascertaining its solidifying-point,

[1] *Wagner's Jahresb.*, 1872, p. 675.
[2] *Arch. Pharm.*, 1886, vol. xxiv., p. 572.

which should be between 15°·5 and 24° C. Having ascertained this temperature, a mixture of carbolic and cresylic acids is made in such proportions as to have the same solidifying-point. This must be adjusted by trial, or a number of standard specimens may be prepared.[1] The exact point of solidification can be observed more exactly if a minute fragment of crystallized carbolic acid be added, to induce the commencement of the change of state: or the sample may be solidified and the liquefying-point noted. As excess of cresylic acid prevents crystallization, it is evident that in some cases a second fractional distillation should be resorted to, the process being arrested when the thermometer rises to 190°.

We may here mention Tidy's and Abel's methods (pp. 554 and 555) for estimating the quantity of "tar-acids" in creosote oil.

Dr Weyl, of Mannheim, tests crude carbolic acid by a caustic-soda solution of sp. gr. 1·263 to 1·297. Stronger alkali extracts substances whose sodium compounds are insoluble in the mixture of liquids, and are precipitated as a heavy layer between the oil and the sodium-phenate solution. The substances (which have not yet been examined) belong to the heaviest constituents of coal-tar.

According to Watson Smith, cresol retains less water of hydration than phenol; hence a superior quality of crude carbolic acid, containing less cresol, gives off more water than an inferior. In the former case up to 16 per cent. of water is found (*cf.* the composition of crude carbolic acid, p. 583).

O. Bach[2] estimates water and phenol in one and the same sample of crude carbolic acid. Fifty c.c. of the acid to be tested are distilled in a retort until solid hydrocarbons begin to deposit in the condenser. The distillate is received in a wide burette, holding 100 c.c. and graduated in $\frac{1}{5}$ c.c., which has a glass cock fused on to its lower end. In this burette is previously placed a saturated solution of common salt, about 25 c.c. in volume, and its level is read off exactly. If the car-

[1] *Cf.* (p. 218) the experiments made by Lunge and Zschokke on the fusing-points of mixtures of pure phenol and pure paracresol. Since "cresylic acid" contains all three isomeric cresols, the indications furnished by Lowe's prescription must be of a very rough character.

[2] *Chem. Zeit.*, 1882, p. 989.

bolic acid be free from water, the distilled oil separates clearly from the salt solution; but if it be aqueous, the oil with the water and brine form a kind of emulsion; by agitating, however, the two layers will quickly appear distinct. The increase in volume of the brine directly indicates the quantity of water contained in the crude acid. Before estimating the phenol, the brine is removed by means of the glass cock. The burette is then filled up to the zero mark with a caustic-soda solution of sp. gr. 1·26, and, after closing with a cork, is vigorously shaken and allowed to settle. If the burette was quite clean and especially free from grease, the oil will have completely separated after half an hour, and its level can be observed. The difference from the volume formerly noted at once gives the amount of phenols.

Toth[1] shakes up 20 c.c. crude carbolic acid with 20 c.c. caustic-potash solution of sp. gr. 1·25 to 1·30, allows to stand for half an hour, and dilutes with water up to 250 c.c., whereupon the tarry constituents of the crude acid separate and are removed by filtration. The residue is washed with tepid water till the reaction has ceased to be alkaline; the filtrate and all the washings are collected and diluted to 3 litres. Fifty c.c. of this solution are taken out, and to this is added 150 c.c. of Koppeschaar's bromine solution (see below), and 5 c.c. of concentrated hydrochloric acid. The mixture is shaken up now and then for twenty minutes, 10 c.c. solution of potassium iodide is added; and, after standing at most five minutes, starch solution is added, and the free iodine titrated with sodium thiosulphate (see below).

This method cannot be accurate, as crude carbolic acid contains a large amount of cresols, which combine with much less bromine than phenol proper, as first shown by Kleinert.[2] Hence Stockmeier and Thurnauer[3] modify the method in the following, at the same time more expeditious, way. They dissolve 1·5 or 2 g. of crude carbolic acid or 1·0 g. of strong carbolic acid in three times its volume of 30-per-cent. caustic-potash solution, by shaking for five or ten minutes in a small flask; this they dilute to a litre, whereupon the hydrocarbons separate very well at the bottom or the top of the aqueous

[1] *Fresenius's Zeit.*, vol. xxv., p. 160. [2] *Z. anal. Chem.*, 1884, p. 1.
[3] *Chem. Zeit.*, 1893, pp. 119 and 131.

liquid. Of the latter a little over 100 c.c. is filtered, and two portions of 50 c.c. each are mixed in a stoppered flask with 100 c.c. of a solution of 2·517 g. sodium bromate and 9 or 10 g. sodium bromide in a litre, together with 5 c.c. strong hydrochloric acid; after standing for ten minutes 15 c.c. of a 12·5-per-cent. KI solution is added, and the whole is titrated with sodium thiosulphate. At the end of the titration, together with starch solution, a little chloroform is added, which prevents the tribromphenols from curdling and thus enclosing some iodine. The presence of aniline and pyridine bases has but little influence.

The same authors examine the phenols separately by extracting them with caustic-potash solution, removing from this solution all hydrocarbons by shaking with ether, precipitating the phenols with dilute sulphuric acid, and distilling them off by means of open steam. The distillate is saturated with NaCl, and the phenols extracted by ether. The latter is driven off again, and the pure cresols are fractionated: 1st, up to 198° or 202°; 2nd, up to 240°; 3rd, above 240° C. Each fraction is separately titrated with bromine, and to reduce the figures to the true percentage of cresols they must be multiplied for the first fraction by $\frac{510{\cdot}63}{444{\cdot}44}$, for the second by $\frac{510{\cdot}63}{x}$, where x denotes the total quantity of bromine calculated for 100 g. phenol. See, however, later on, the statements of Ditz & Cedivoda, who declare the principle of this analytical method to be erroneous.

Vaubel[1] pointed out that paracresol does not fix three, but only two atoms of bromine; Stockmeier and Thurnauer contend[2] that this does not affect their method and at most proves that their carbolic acids had contained little or no paracresol [?].

The *percentage of water* in phenol, according to Vulpius,[3] can be approximately tested by adding olive oil. Carbolic acid, free from water or containing but little water, can be mixed with many times its own volume without becoming turbid. The more water it contains, the less oil it will take without becoming turbid. Four volumes of crude carbolic acid containing not much above 10 per cent. water will give a clear mixture after

[1] *J. prakt. Chem.* [2], xlviii., p. 74. [2] *Chem. Zeit.*, 1893, p. 404
[3] *Wagner-Fischer's Jahresber.*, 1884, p. 494.

being well shaken up with 4 parts of olive oil; a fifth part of oil will cause strong turbidity.

Riesenfeld (*Chem. Centr.*, 1902, ii., 627) estimates the percentage of water in phenol by the electric conductivity of a solution of potassium iodide in the product to be tested.

Casthelaz [1] gives the following notes on the testing of crude and impure (liquid) carbolic acids:—"Crude carbolic acid" is a dark-brown or black fluid, containing phenol, cresol, saponifiable oils, non-saponifiable oils, naphthalene, water, and ammonium sulphhydrate. Its percentage in crystallizable phenol is estimated by Lowe's method (*cf.* above); "crude carbolic 60 per cent." means an acid which by Lowe's test indicates 60 per cent. of real phenol.—"Liquid carbolic 100 per cent., 95 per cent., 50 per cent." (not to be confounded with "liquefied pure carbolic acid," *cf.* below) mean an article containing the above percentages of cresol, for those acids do not contain more than traces of real (crystallizable) phenol. They have a more or less unpleasant smell, due to sulphuretted hydrogen, ammonium sulphhydrate, or organic bases. These sulphur compounds are easily detected by shaking up with water and adding subacetate of lead, which produces a more or less abundant black precipitate of lead sulphide. The sulphur compounds can be removed from phenol by agitating it with a solution of sodium bisulphite; the latter is changed into thiosulphate (Casthelaz's patent, 1881). The more or less deep colour of liquid carbolic acid depends upon the washings practised with the crude acid before redistillation. The more bases have been left in it, the darker the acid will turn with age. —The liquid carbolic acids at 95 and 90 per cent. contain 5 or 10 per cent. of water; "liquid carbolic acid 50 per cent." is an artificial compound, which appears in the market only in times of scarcity. It ought to contain 50 per cent. cresylic acid and saponifiable oils, 40 per cent. heavy and light, not saponifiable tar oil, and 10 per cent. water; but recently articles have been sold under the name by English and German manufacturers which did not even contain 30 per cent. saponifiable oils.

Instead of the ordinary soda test, Casthelaz proposes the following tests:—

1st. Shake up 50 c.c. liquid carbolic acid with 50 c.c. of

[1] *Bull. Soc. Chim.*, vol. xlii., p. 574.

water. The volume of the carbolic acid should remain almost the same; if not, it contains alcohol, glycerin, carbolate of soda, etc.

2nd. Shake up 50 c.c. of the liquid carbolic acid with 50 c.c. of sulphuric acid, diluted with 50 per cent. water. Any slight diminution of the volume of carbolic acid corresponds to its percentage of water. If the diminution of volume is considerable, there is probably carbolate of soda present; and the insoluble upper layer indicates the quantity of cresylic acid and other saponifiable products.

3rd. 100 c.c. liquid carbolic acid is mixed with 100 c.c. caustic-soda solution of sp. gr. 1·38, and diluted with water up to one litre. This will separate the non-saponifiable products; the naphthalene floats at the top in the solid state, and can easily be collected and weighed.

4th. 100 c.c. are distilled in a tubulated retort, the thermometer reaching down to within 1 cm. ($\frac{3}{8}$ in.) from the bottom. Notice is taken, 1st, of the water coming over before the cresol; 2nd, of the oily product distilling between 182° and 190°, and consisting mainly of phenols; 3rd, of the percentage distilling between 190° and 205°, = cresol; 4th, of the residue remaining in the retort.

The test of the *German Pharmacopœia* for "90-per-cent. crude carbolic acid" is as follows:—Shake 9 volumes of caustic-soda liquor of sp. gr. 1·079 to 1·08 very thoroughly with 1 volume of crude phenol and allow to settle perfectly; the portion remaining insoluble, which floats on the top and which is liquid or semiliquid, ought not to exceed 10 per cent. by volume. The product reprecipitated from the alkaline solution by adding hydrochloric acid, in the case of a good article (not containing an excess of cresol), should be soluble in at most thirty parts of water.

Hager tests crude phenol of no less than 85 per cent. by shaking 10 c.c. with 20 c.c. glycerin, heating gently, shaking again, and allowing to settle for six or ten hours. The lower, lighter layer is a solution of the phenols in glycerin; the upper, darker one consists of the impurities.

Naphthalene in crude carbolic acid is estimated by Muter (*Chem. Centr.*, 1890, i., p. 840) by shaking 50 c.c. of the sample with 200 c.c. of a 10-per-cent. solution of caustic soda, which

leaves the naphthalene behind. It is filtered, washed with water, pressed and weighed. [Of course this process holds good only for the very exceptional case that no tar oils are present, which would keep part of the naphthalene dissolved.]

Seiler (*Schweiz. Wochensch. f. Pharm.*, 1892, p. 365) heats 100 g. crude carbolic acid with 100 g. milk of lime (1 : 5) for an hour on the water-bath, with stirring adds 100 c.c. water, and filters after cooling. In so-called 40 to 45 per cent. commercial carbolic acid he found only 3 to 5 per cent. phenols. [This method is utterly worthless, as was also shown by Klisch (*Pharm. Zeit.*, 1892, p. 650) and Roos (*ibid.*, p. 666).]

Lehmann[1] extracts with caustic-soda solution, and afterwards the non-saponifying oils with petroleum spirit.

Schacherl[2] extracts several times with caustic-soda solution of sp. gr. 1·1, dilutes the solutions with the same volume and water, and distils until the distillate is quite clear and free from oil. The residue, after cooling, is acidulated with HCl and again distilled. The water separating from the distillate is distilled over again, till quite clear, and the phenol separated from all these solutions by sodium chloride. [This is not altogether an exact method.]

C. E. Smith[3] describes a somewhat complicated process for applying the bromine method to the examination of crude carbolic acid, which cannot give very accurate results.

Schryver[4] points out that all bromine or iodine methods must be wrong in the presence of hydrocarbons reacting upon Br or I. His own method is founded on the evolution of NH_3 from sodium amide by hydroxyl compounds:

$$NaNH_2 + C_6H_5OH = NaOC_6H_5 + NH_3.$$

About 1 g. of powdered sodium amide is washed with pure benzene (free from thiophen) and is then placed, together with 50 or 60 c.c. pure benzene, in a wide-necked flask, connected with a reflux-cooler, a drop-funnel, and an aspirator. It is heated to boiling on a water-bath, and the NH_3 adhering to the amide is removed by aspiration. Now the sample to be tested, dissolved in 6 parts pure benzene and completely dried with

[1] *Chem. Zeit.*, 1892, p. 365. [2] *Pharm. Centralhalle*, 1892, No. 2.
[3] *Amer. J. Pharm.*, 1898, p. 369; *Chem. Zeit.*, 1898, p. 230
[4] *J. Soc. Chem. Ind.*, 1899, p. 553.

fused sodium acetate, is run in through the drop-funnel, a receiver with 20 c.c. normal sulphuric acid having been interposed between the apparatus and the aspirator. The boiling is continued, air being always aspirated through and the funnel being well rinsed with benzene, until all NH_3 is evolved, which takes about an hour and a half. It is indispensable that the apparatus should be absolutely dry. By titrating the acid in the receiver, the phenol can be estimated to + 2 per cent. In mixtures of phenol and cresol the "hydroxyl number" thus found permits of calculating the mutual proportion of both to about 10 per cent. In order to estimate the *water*, the phenols are dissolved in benzene, dried with dehydrated acetate, and the phenol estimated as above.

Fischer and Koske, in *Süd. Chem. Zeit.*, 1903, No. 21, describe a number of samples of "crude carbolic acid" which consisted mainly of cresols, as proved by fractionating, etc.

Recently crude carbolic acid has sometimes been found adulterated with the phenoloid substances from blast-furnace tar, which chemically are much nearer to the complicated phenols of wood- and lignite-tar. Possibly their antiseptic properties equal those of the coal-tar phenols, but at all events they should not be added to these without informing the buyer thereof.

Analysis of Pure Carbolic Acid.

The properties of chemically pure phenol have been described, pp. 209 *et seq.* and the qualitative reactions on p. 213. Ordinary commercial "pure" carbolic acid may contain traces of fixed substances—compounds of sodium, calcium, copper, lead, etc., but never more than in most minute quantity. More usually there are present small quantities of higher-boiling phenols, of substances which cause the development of a red or yellowish-brown colour (pp. 213 and 596 *et seq.*), and of water. Crystallized phenol may contain as much as 5 per cent. water; only when containing 7 per cent. and upwards of water, carbolic acid remains liquid at ordinary temperatures. Water lowers the fusing-point of phenol, but it increases its solubility (perhaps the statements of Allen, ascribing to phenol a greater solubility than that found by all other observers, p. 211, may be explained in this manner). Even 1 per cent. of water may be recognized by shaking the phenol with its own volume of

chloroform or ether, which in that case will produce a milky liquid. The quantity of water can be approximately tested by the increase in volume of a concentrated solution of sodium chloride or calcium chloride, as has been described above in connection with the testing of crude carbolic acid. The quantitative estimation of the water can be exactly performed by mixing the phenol with about five times its weight of finely levigated lead oxide, and drying at 70° or 80° till the weight is constant, or by Schryver's method, p. 614; *cf.* also pp. 609 and 611.

One of the most important tests for the purity of carbolic acid is its fusing-point. About this, *cf.* p. 210. The German Pharmacopœia requires a fusing-point of 40° to 42° C.; but several authorities recently demand that not the melting-point, but the *solidifying-point* should be fixed, and that at 39° to 41° C., and this would seem to be the general opinion of practical men at the present time. The solidifying-point is found as follows. Take a real average sample of the lot (which will necessitate liquefying a larger portion, with careful exclusion of all moisture), place about 50 g. in a wide-mouthed bottle and allow it to cool very slowly, constantly stirring with a thermometer showing tenths of a degree C. When the solidifying-point has been nearly reached, the temperature ought not to fall more than 0·5 in the course of a minute. The solidifying-point is that at which a small crystal of pure phenol, introduced into the liquid, just begins to grow. If the cooling had been carried too far, the temperature rises again when a strong crystallization sets in, and the highest point now reached is the real "solidifying-point." (Kraemer and Spilker.)

Eger (*Pharm. Zeit.*, 1903, p. 210; *Chem. Zeit. Rep.*, 1903, p. 86) contends that the fusing-point of carbolic acid = 40° to 42° C., as demanded by the German Pharmacopœia, is decidedly too high. The purest obtainable phenol solidifies at 40·9, and its fusing-point is at most 0·1° higher. Hence the fusing-point should be put at the highest at 41°, better at 39° to 41°.

He further states that liquefied carbolic acid should be tested as follows:—10 c.c. should at 15° not be rendered cloudy by adding 2·3 c.c. water, but by the further addition of 8 to 10 drops of water. This cloudy solution should form a clear solution by the addition of not less than 115 and not more than 135 c.c. of water.

The higher-boiling phenols greatly lower the fusing-point of carbolic acid. This is most clearly proved by the experiments of Lunge and Zschokke (*cf.* p. 218), which prove such a lowering of the fusing-point, even when the second phenol is paracresol, whose fusing-point is as high as 32°·5. But since commercial carbolic acid contains even larger proportions of metacresol, which is liquid far below the ordinary temperature, the lowering of the fusing-point is far more considerable than would be indicated by those experiments. The reddish or brownish liquid collecting in the vessels where not absolutely pure phenol is kept mostly contains those higher phenols. Carbolic acid, free from these, even when containing several per cent. of water, after heating for some time in an open dish and cooling down in a desiccator over concentrated sulphuric acid, solidified to a white crystalline mass, with a melting-point of about 30°; but if it contains a little cresol, etc., the residue is brown, and has a much lower melting-point, sometimes remaining liquid. Some authorities assume that these very substances cause the reddening of phenol by an oxidizing process (p. 213). They are also indicated by agitating phenol with three times its bulk of pure concentrated sulphuric acid, to which they impart a yellow, brown, or pink colour; also by forming a muddy mixture with glycerin, and by furnishing with bromine a product distinct from pure tribromophenol by not being crystalline, by being coloured, and by fusing below 90°. (*Cf.* also Allen's table of the differences in the behaviour of carbolic and cresylic acids, p. 216.)

Pure carbolic acid should dissolve completely in 4 vols. of 10 per cent. caustic soda or potash solution, forming a perfectly clear liquid which is not rendered turbid by addition of water. An even more delicate test is the solubility in water; 1 part pure phenol should dissolve in 15 parts of distilled water of 15° C. to a perfectly clear liquid.

When fused, pure phenol is as limpid as water and perfectly colourless, and on solidifying it should form a white or glassy translucent mass. But in course of time even the purest phenols turn red; *cf.* pp. 213 and 596.

Crystallized carbolic acid ought in no case to contain any sulphur compounds, which impart to it a nauseous smell, and which can be detected by adding subacetate of lead (p. 600),

or by boiling an alcoholic solution of the sample with lead hydroxide.

Liquefied pure carbolic acid—that is, pure phenol purposely liquefied by the addition of 10 per cent. water, alcohol, or glycerin—can be distinguished from "liquid carbolic acid," which essentially consists of cresols, etc. (p. 601), by its boiling-point (beginning at or below 100°, but quickly rising to 185 to 190°, whilst the last-mentioned article boils at 185 to 209°), by its solubility in water (the liquefied pure acid requires *at most* 18 parts of water to form a clear solution, while cresylic acid is not completely dissolved even by 50 parts of water), by the different properties of the bromine precipitates, and by all the other distinctive reagents mentioned (p. 216). Its percentage of pure phenol is determined by one of the methods described below.

Schlickum[1] founds a method on the increase of volume produced in liquefied carbolic acid by shaking with its own volume of water. This method is accurate, but the measurement should be made very correctly, as a difference of 1 c.c. is =8 to 10 per cent. of water.

Vulpius proposed another somewhat similar method, which has been worked out in detail by Salzer.[2] He also points out that, whilst anhydrous phenol gives a clear mixture with carbon disulphide, aqueous phenol yields a milky liquid, which requires all the more acid to clear it the more water the phenol contains (*cf.* p. 519). Later on (*Pharm. Centr.*, 1891, p. 153), Salzer described another test for liquefied carbolic acid: 10 c.c. must not give a permanent turbidity with 2·3 cm. of water; with more water, the sample must yield a turbid mixture which dissolves to a clear liquid with not less than 135 and not more than 140 c.c. water.

Small quantities of cresol are not indicated by these methods; *cf.* Beckurts (*Arch. d. Pharm.* [3], vol. xxiv., p. 580).

The exact *quantitative estimation of phenol* is always made by precipitating it with bromine as tribromphenol, a reaction discovered in 1871 by Landolt. Tribromphenol forms white star-shaped groups of needles, of a peculiar smell, fusing at 95°, insoluble in water, acids, or somewhat dilute alcohol, but soluble in alkalis, ether, or absolute alcohol. Hence it is necessary to

[1] *Pharm. Zeit.*, 1884, p. 794. [2] *Ibid.*, 1886, No. 1.

acidify the phenol or its solution in water or dilute alcohol, and to add bromine-water till the liquid has assumed a permanent yellow colour. It is best to heat the liquid till the precipitate fuses to an oil, and then to cool it; the precipitate thus solidifies to a cake, which is easily washed, dried, and weighed. If much cresol is present (which also gives a tribrom-derivative, though a liquid one), the precipitate will be a sticky mass. It is therefore not possible to separate phenol from cresol by this method. One hundred parts $C_6H_2Br_3(OH)$ correspond to 28·4 $C_6H_5(OH)$; and the quantity of bromine which indicates 1·000 phenol would indicate 1·106 cresol. As a *gravimetric* method, however, this test is not correct, for Weinreb (*Monatsh.*, 1885, p. 506) has shown that the precipitate is not $C_6H_3Br_3O$, but $C_6H_3Br_3OBr$; but the additional bromine in titrating sets iodine free from KI, so that Koppeschaar's volumetric method is exact after all. Beckurts (*Arch. d. Pharm.*, 1886, vol. xxiv., p. 561) confirms this.

The gravimetrical estimation of phenol by this method is, moreover, much hampered by the fact that the tribromphenol is rather volatile at 100.° But the formation of that compound can be turned to account for an accurate *volumetrical* estimation, which was first proposed by Koppeschaar.[1] We here describe his method, which is still mostly employed. The liquids required are—

1st, a solution of sodium thiosulphate, exactly corresponding to a solution of iodine, containing 5 g. I per litre;

2nd, solution of starch;

3rd, bromine-water of such concentration that 59 c.c., after being decomposed with potassium iodide, require 18 to 20 c.c. of the thiosulphate solution;

4th, a solution of potassium iodide, containing 125 g. per litre.

Dissolve 4 g. of the sample of carbolic acid in water, and dilute up to 1 litre. Put 25 c.c. of this solution into a stoppered half-litre flask, fill it quickly up to the mark with bromine-water, close it and agitate for some time. Before adding the bromine-water, run 50 c.c. of the same into a small beaker, containing 5 c.c. of the potassium-iodide solution. After standing for half an hour, empty the contents of the half-litre flask into a large beaker, already containing 5 c.c. of the potassium-iodide

[1] *Z. anal. Chem.*, 1876, p. 233.

solution, and rinse the flask twice into the same beaker. Then titrate the liquids, both in the small and the large beaker, with the thiosulphate solution, adding some of the starch solution, but only towards the end of the operation, and read off, when the blue colour ceases to return after a few minutes.—We have thus employed 25 c.c. of the phenol solution (corresponding to 0·1 g. of the sample), we have added 475 c.c. bromine-water, and we have standardized 50 c.c. of the latter with a thiosulphate solution of the strength formerly indicated. If we call a the c.c. of thiosulphate required for the 50 c.c. of bromine-water, and b the c.c. of thiosulphate required for the excess of bromine in the 25 c.c. of the solution, the formula

$$(9{\cdot}5\ a - b)\ 0{\cdot}61753$$

directly indicates the percentage of phenol in the sample.

Koppeschaar also mentions that, instead of bromine-water, a mixture of five molecules of sodium bromide and one molecule of sodium bromate may be employed. This mixture is obtained by adding to a solution of caustic soda an excess of bromine and evaporating to dryness. The resulting mixture of salts is redissolved, and, on adding hydrochloric acid, yields all its bromine in the free state:

$$5NaBr + NaBrO_3 + 6HCl = 6NaCl + 6Br + 3H_2O.$$

It is, however, not necessary to evaporate the original mixture to dryness; it is sufficient to boil the solution of bromine in caustic soda for some time. Allen[1] has proved that a boiled solution of this kind keeps its standard for a long time. He had himself formerly[2] proposed employing this solution in lieu of bromine-water, and obtaining its standard by calculation, by employing a standard solution of caustic soda for preparing the mixture; but this very indirect method introduces an element of uncertainty, and seems less trustworthy than Koppeschaar's original method, which is also preferred by Waller.[3]

[1] *J. Soc. Chem. Ind.*, 1884, p. 64.

[2] *Commercial Organic Analysis*, 1879, vol. i., p. 307.

[3] *Chem. News*, xliii., p. 152. The figures given by Allen for calculating the results, which were repeated in the first edition of the present work, are wrong. Every c.c. of the thiosulphate solution used over and above 6·17 c.c. indicates 0·00157 g. impurities in 0·1 g. of the sample, or 1·57 per cent.

It seems the most certain method to standardize the bromine-water with pure phenol itself. This has been recommended by Diacosa,[1] and is also employed by Allen in his last prescriptions for determing the phenol in carbolic soap (see below). Diacosa runs the aqueous solution of phenol into the bromine-water, and determines the end of the reaction by testing a drop of the clear solution with paper soaked in a solution of starch and potassium iodide. This plan was first proposed by Degener.[2] Chandelon[3] uses the same indicator; but he employed the brominated caustic soda in lieu of bromine-water. These direct tests are quite incorrect, owing to the formation of tribromphenol-bromide (p. 619).

Beckurts (*cf.* above) proposes the following as the most certain mode of testing. The solutions employed are :—

1st. A $\frac{1}{100}$ normal solution of potassium bromide, containing 5·939 g. KBr per litre.

2nd. A $\frac{1}{500}$ normal solution of potassium bromate, containing 1·6666 g. $KBrO_3$ per litre.

3rd. A solution of 125 g. potassium iodide per litre.

4th. A $\frac{1}{10}$ normal solution of sodium thiosulphate, containing 12·4 g. of $Na_2S_2O_3$, 5 aq., per litre, and equal to 0·008 g. bromine or 0·00156 g. phenol per cubic centimetre.

Into a well-stoppered bottle put 25 to 30 c.c. of the solution of phenol (1 : 1000), add 50 c.c. each of the solutions of KBr and $KBrO_3$, then 5 c.c. concentrated sulphuric acid, and shake vigorously. After ten or fifteen minutes add 10 c.c. of the KI solution, and titrate the iodine which separates with the thiosulphate solution. This process is accurate whenever solutions of *pure* carbolic acid are to be tested, or mixtures from which such can be isolated, but it fails in the case of crude carbolic acid or other mixtures where cresol is present.

Moerk (*Chem. Centr.*, 1904, ii., p. 1764) recommends as indicator in Koppeschaar's method chloroform in lieu of starch solution, the final reaction being sharper. L. J. Lloyd (*ibid.*, 1905, i., p. 599) describes his special way of carrying out that method, by which he believes to attain an accuracy up to 0·1 per cent.

Since the higher-boiling phenols are much less soluble in

[1] *Rep. analyt. Chem.*, ii., p. 137 ; *J. Soc. Chem. Ind.*, 1802, p. 203.
[2] *J. prakt. Chem.*, [2] xvii., p. 390.
[3] *Bull. Soc. Chim.*, vol. xxxviii., p. 69.

water than real carbolic acid, or even insoluble, the direct application of Koppeschaar's method, as will be easily understood, yields very unsatisfactory results with creosote oils containing such higher phenols.[1] In this case the phenols may be dissolved in caustic-soda solution, and this solution may be titrated with bromine-water in the presence of an excess of acid; but in the best case only approximate results can be thus obtained, especially since the calculating factor for the higher-boiling phenol is quite different from that for carbolic acid (see p. 620).

Leube's colorimetric method, with employment of ferric chloride,[2] and Nietsch's method of converting the phenols into sulphonates of barium or lead and estimating those metals,[3] can evidently not yield any accurate results. The same holds good of the proposal of Carré, to convert the phenol into picric acid and estimate this colorimetrically.[4] Bader[5] makes a solution of not less than 20 g. phenol per litre, of which 50 c.c. is titrated with standard soda solution, employing as indicator a solution of the symmetrical trinitrobenzenes. The liquid must be completely colourless to begin with, and the end is shown by a reddish-yellow colour. This process can hardly yield satisfactory results.

Messinger & Vortmann[6] employ an iodometrical process. They dissolve 2 or 3 g. of phenol in at least 3 molecules caustic soda (in solution), dilute to 250 or 500 c.c., heat 5 or 10 c.c. to 60°, and add decinormal iodine solution until the liquid has turned strongly yellow, when on shaking a red precipitate of iodophenols is formed. The cool liquid is acidulated with dilute sulphuric acid, diluted to 250 or 500 c.c., and 100 c.c. of this is titrated back with decinormal thiosulphate. Each 6 molecules of iodine used = 1 molecule phenol.

Korn[7] applies this process to the estimation of phenol in sewage.

Wake and Ingle[8] discuss the iodine values of the various phenols, which differ very much from one another.

[1] Cf. *Z. anal. Chem.*, xxiii., p. 1 (Kleinert).
[2] *Dingl. polyt. J.*, ccii., p. 308.
[3] *Wagner's Jahresber.*, 1879, p. 1036.
[4] *Comptes rend.*, 1891, p. 139.
[5] *Z. anal. Chem.*, 1892, p. 58.
[6] *Berl. Ber.*, 1890, p. 2753.
[7] *Z. anal. Chem.*, xxxiii., p. 552.
[8] *J. Soc. Chem. Ind.*, 1908, p. 215.

Storch[1] gives a cryoscopic method for estimating water and orthocresol in crystallised carbolic acid, which can at the best yield only approximate results.

Keppler[2] proposed extending Koppeschaar's method to the estimation of pure cresols, starting on the assumption that they fix three atoms of bromine, which is quite wrong, as already pointed out by Vaubel,[3] and more in detail by Ditz and Cedivoda.[4] They show that metacresol with an excess of bromine forms a tetrabromide, whilst orthocresol fixes only two atoms of bromine. Up to the present, an accurate method for separating phenol and the three cresols does not exist. *Cf.* also Vaubel (*Z. angew. Chem.*, 1899, p. 1031) and Ditz (*ibid.*, p. 1155).

Muter[5] proves the presence of water in cresols by shaking the sample with three volumes of a saturated solution of sodium chloride. Anhydrous cresol absorbs about 5 per cent. of the latter; but if the cresol is already saturated with water, the volume of the salt solution is not changed.

Tocher (*Pharm. J.*, lxvi., 360) estimates phenols, in the absence of other oxidizable substances, by a decinormal solution of potassium permanganate. The solution of phenol (1 : 100) is mixed with an excess of sodium bicarbonate, the permanganate is added, and the whole boiled for a few minutes. After cooling, dilute sulphuric acid is gradually added till the reaction has turned acid; the liquid is warmed up and titrated back with decinormal oxalic acid. Each 0·01 g. pure C_6H_6O takes 29·78 c.c. decinormal $KMnO_4$.

Reuter (*Chem. Centr.*, 1905, i., 1012) tests pure carbolic acid for the presence of phosphoric acid and tin salts; the former might have been added to prevent reddening, and the latter might have been taken up from the containing vessels.

Analytical Methods for estimating the Three Isomeric Cresols.

For this purpose Raschig (*Z. angew. Chem.*, 1900, 759) has worked out the following process. Weigh off exactly 10 g. of the cresol mixture in a small Erlenmeyer flask. Add 15 c.c. of sulphuric acid, sp. gr. 1·38. Keep for an hour in a steam

[1] *Berl. Ber.*, xxvii., referate p. 90.
[2] *Arch. Hyg.*, xviii., p. 51.
[3] *J. prakt. Chem.* [2], xlviii., p. 74.
[4] *Z. angew. Chem.*, 1899, pp. 873 and 897.
[5] *Chem. Centr.*, 1890, i., p. 840.

oven; then pour into a wide-necked litre flask, cooling this on the outside under a water-tap; this will cause the sulphonic mixture to spread as a syrup on the sides of the flask. Put 90 c.c. nitric acid (sp. gr. 1·4) into the Erlenmeyer, shake it to dissolve the remains of the sulphonic mixture left therein, pour the whole quickly into the litre flask and shake this vigorously till all the sulphuric acid is dissolved, which should be the case in about twenty seconds. Place the flask at once under a draught hood. Very soon a violent reaction sets in. The liquid boils vividly, red vapours escape and oily drops of trinitrocresol separate. After ten minutes standing pour the contents of the flask into a dish already containing 40 c.c. of water, and rinse it with another 40 c.c. water. The trinitrocresol now solidifies, with escape of nitrous vapours. Leave all to cool for two hours, then squash the mass with a pestle and put it on to a vacuum filter. When the liquid portion has passed through, wash the filter with 100 c.c. water, dry at 95° to 100° and weigh, using a filter-paper of the same size as counterpoise. Such a test takes about five hours, and ten to twenty tests may be made at the same time. Ten g. pure metacresol in this manner gives exactly 17·4 g. of the nitro-product, and mixtures of all three cresols give exactly 1·74 part of the nitro-product for each part of *m*-cresol present. In the presence of less than 10 per cent. phenol this process is still quite accurate, but when more than 10 per cent. C_6H_6O is present, it does not work. Such mixtures are, however, not often found in commerce, and they would in any case be recognised by the boiling-points. Xylenols act in the same manner; in their presence the nitro-product does not properly solidify.

Raschig's process is exact up to 1 per cent., and as a method for practical working seems to fulfil all purposes, but it takes about 5 hours of work, wherefore Ditz (*Z. angew. Chem.*, 1900, p. 1050; see below) prefers the method worked out by him and Cedivoda.

A discussion on the accuracy of Raschig's process has been carried on in 1908 by Herzog (*Chem. Centr.*, 1908, p. 405); Raschig (*ibid.*, p. 973); Herzog (*ibid.*, p. 1214). *Cf.* also Fortmann in *Chem. Zeit.*, 1908, p. 118, who entirely approves of Raschig's process.

Russig and Fortmann[1] describe a similar process for

[1] *Z. angew. Chem.*, 1901, p. 157.

estimating metacresol in mixtures of cresols which takes more time than the foregoing, but is claimed to yield more accurate results. Weigh 50 g. cresol in an Erlenmeyer. Add 150 c.c. sulphuric acid (1·84 sp. gr.), and allow to stand for 1 or 2 hours without applying outside heat. For nitrating employ a tubulated glass retort, holding 1 litre, placed on a sand-bath; connect its downward branch with a good chimney-draught, interposing a wash-bottle. Put 400 c.c. nitric acid (1·38 sp. gr.) into the retort, heat it up to 60° C., and remove the flame. Close the tubule of the retort by a perforated indiarubber stopper, through which passes the tube of a cylindrical drop-funnel. This must be wide enough to receive the neck of the Erlenmeyer when this is quickly reversed into the funnel, where it is left during the operation. Now allow the sulphonic acid to enter into the hot nitric acid, drop by drop, which should take 1½ or 2 hours. Much heat is developed, and copious nitrous vapours are given off. After standing for another 20 minutes, pour the contents of the retort into a roomy porcelain dish containing 200 c.c. water, and rinse the retort with another 200 c.c. of water. Allow to stand till the next day, squash the cake left in the dish with a porcelain spatula, and collect the trinitro-cresol in a hardened filter on a vacuum pump. Another 200 c.c. water is used for rinsing the dish and the crystals. These are dried in a steam oven at 95° to 100° C., and weighed. In this way you obtain from perfectly pure *m*-cresol 175·6 per cent. of the trinitro-product, against 174·0 by Raschig's plan.

Already, in 1899 (*Z. angew. Chem.*, 1899, pp. 873, 897), Ditz and Cedivoda had worked out a volumetric process for estimating metacresol in a mixture of the cresols. To this they draw attention again in 1900 (*ibid.*, 1900, p. 1050), and they defend it also against an attack made upon it by Russig and Fortmann in their just-quoted paper in 1901 (*ibid.*, 1901, p. 160). Their process is based on the difference of behaviour of the isomeric cresols against a brominating mixture. It is claimed to give very accurate results in a short time, but it requires the *complete* absence of phenol and of xylenols; in this respect the process of Raschig or Russig has the advantage over it. Ditz and Cedivoda weigh off 1 g. cresol, dissolve in water, with a little caustic soda, and dilute to 250 c.c. Of this solution they bring two samples of 25 c.c. each into stoppered bottles, add a

sufficient quantity of Koppeschaar's bromide-bromate solution, then 10 c.c. of hydrochloric acid (1 : 1), shake exactly one minute and add 20 c.c. of a 5 per cent. solution of potassium iodide. After standing 1 hour, the separated iodine is titrated with thiosulphate, the quantity of which corresponds to the bromine taken up. If you call the quantity of metacresol originally present x, the sum of ortho- and paracresol y, a the weight of cresols employed, and b that of the bromine absorbed, the two equations: $x+y=a$, and

$$\frac{3\mathrm{Br}\,x+2\mathrm{Br}\,y}{108{\cdot}08}$$

allow to infer the quantity of metacresol to be

$$x=a-y=a-\frac{2{\cdot}2195\,a-b}{0{\cdot}7397}=\frac{b-1{\cdot}4798a}{0{\cdot}7397}.$$

The results are accurate up to 0·5 per cent.

Uzt (*Chem. Centr.*, 1906, ii., p. 1286) finds the refractive index of the crude cresol (mixture of all three isomers) = 1·5414 to 1·5444; that of the three isomers: $o=1{\cdot}5492$, $m=1{\cdot}5402$, $p=5415$, all at 15° C. Genuine lysol (p. 631) = 1·5068.

Applications of Carbolic Acid.

In the pure state phenol is employed in the manufacture of artificial colours, especially of picric acid and corallin; these are not very much used as colours now, but picric acid and its salts are extensively utilized in the manufacture of explosives, such as "melinite" and "lyddite," and probably the greater part of the carbolic acid produced at present finds its way into the explosives factories. Also some azo-colours have been made with it; and undoubtedly many other applications of it and its homologues will follow in this direction. But it is very doubtful whether it will ever pay to employ phenol as a starting-point for preparing rosaniline, as has been proposed. Phenol is also the starting-point for the manufacture of salicylic acid, and a good deal is used for this purpose.

Carbolic acid is also used for antiseptic purposes, but mostly in the crude state, or at least not so pure as for the purposes just named, which indeed would be quite superfluous. For disinfecting sewers, stables (in the case of cattle-diseases), or

even human dwellings, the cheaper descriptions, which are liquid and contain cresol, are probably as valuable as crystallized phenol, and also for preserving hides, bones, etc., for sea transit. The preservation of wood by pickling with creosote oil is founded, at least partially, on the same principle. The preservation of meat in the same way has often been proposed, but does not appear to be practicable, owing to the very tenaciously retained smell and taste of carbolic acid. Beetroot juice can be preserved by it, as shown by Cunisset (*Bull. Soc. Chim.*, 1874, xxi., p. 47) and Hulwa (*Wagner's Jahresber.*, 1875, p. 795). Maercker (*ibid.*, 1872, p. 826) recommends it for destroying the lactic-acid ferment in the manufacture of alcohol.

Kellner (*Chem. Zeit.*, 1884, p. 122) found that carbolic acid is a good remedy for the parasitic diseases of plants and animals; manure containing 2 per cent. of it is harmless to the plants, except when put on the field together with the seed.

Carbolic acid is very important for preserving skins; Kletzinsky (*Wagner's Jahresber.*, 1864, p. 601) showed that it possesses tanning properties; and Baudet (*ibid.*, 1870, p. 669) obtained a patent for this purpose.

Harcke (Ger. Ps. 16022 and 19633) adds carbolic acid in the currying process to the usual mixture of alum and salt; he also makes "artificial leather" by treating fabrics first with a solution of glue and then with a mixed solution of alum, salt, and carbolic acid. Shaw (Ger. P. 27270) and Beda (B. P. 16647, 1886) proceed in the same manner.

For medical purposes, especially for internal use, as well as for Lister's antiseptic treatment of wounds, and for cleaning the instruments, hands, and clothes, the purest crystallized acid is always preferred, both on account of its higher solubility and its less unpleasant smell, which can be entirely masked by a little oil of geranium.

Crude sodium carbolate is employed as a protection against dry-rot, under the name of "house preservatory."

The Hüstener Gewerkschaft (*Z. angew. Chem.*, 1889, p. 132) manufacture basic lining stones for converters by melting powdered chrome iron-ore, limestone, dolomite, and magnesia with sodium phenolate, free from oils.

The Neue Augsburger Kattunfabrik (Ger. P. 95692) employs

a weak solution of phenol (1 : 4000 water) in calico-printing for removing the gum.

Gassmann and the Usines du Rhône (Ger. P. 99756) employ phenol and cresols for dissolving colouring-matters insoluble in water.

Justin Mueller (*Bull. Soc. Ind. Mulhouse*, vol. 76, p. 72) finds that an addition of phenol to the colours for printing on wool has the same effect as chlorinating the wool.

Statistical.

Germany imported and exported the following quantities of pure and crude phenol during the last few years. The importation is nearly all from Great Britain (*Chem. Ind.*, 1908, p. 517).

	1904.	1905.	1906.	1907.	
Importations—					
Altogether . .	5266	5536	5210	5277	tons.
From Great Britain .	5110	5315	4905	4954	„
Exportations—					
Altogether . .	3898	2158	3876	3561	„
To the United States	706	466	534	1047	„

Germany in 1907 imported and exported—

	Tons.	Tons.
Crude and pure phenol	5277	3561
Cresols. . .	3	410

Carbolic Acid and Cresol Preparations.

The widely extended use of carbolic acid and its homologues has led to their being produced in various forms, adapted to special purposes. We shall enumerate only those actually manufactured on a large scale, so far as they have not yet been mentioned before. They are almost exclusively disinfectants and preserving agents.

Preparations containing Soap.

The most important preparations of the phenols are combinations with soap. There is a pretty general agreement on the point that such combinations have a stronger disinfecting power than the phenols by themselves.

According to Engler and Dieckhoff,[1] already in 1874 solutions of soap in tar oils, or of tar oils in soap, were found in the trade.

[1] *Arch. Pharm.*, 1892, part 8.

Such solutions form with water an emulsion in which the tar oil is in the state of finest division, or they are even completely soluble. The first manufacturer whose preparations were scientifically examined was I. Schenkel, of Eisenbüttel,[1] in 1884; but it was only in 1887, when the *Creoline* of Jeyes was extensively advertised by Messrs William Pearson & Co., of Hamburg (hence called "Creoline Pearson"), that these articles became generally known (Ger. Ps. 65387, 65533 to 65537).

Creoline (also sold as cresolin, desinfectol, etc.) is a dark-brown, syrupy liquid, smelling of creosote, sp. gr. 1·04 and 1·08, soluble in every proportion in dilute spirit of wine (1 : 7), ether, and chloroform, partially in petroleum spirit, but insoluble in methylic alcohol. With water it forms an emulsion, most perfectly in the proportion of 2·5 per cent. creoline, of faintly alkaline reaction; it makes no spots and is not poisonous, even when 5 per cent. strong. With acid or alkaline water, or with glycerin, more darkly coloured emulsions are formed. Creoline is used in the same way as carbolic acid. The first persons who recognized Pearson's creoline as a soapy tar-oil solution were Otto & Beckurts;[2] the results of Sprenger,[3] in the main agree with theirs, as proved by the following table. According to this, creoline is nothing but a mixture of creosote oil with a soda-rosin soap and water.

	Otto & Beckurts.	Sprenger.
Hydrocarbons	59·60	44·94 per cent.
Phenols	10·40	12·67 „
Pyridine bases	0·80	2·76 „
Abietinic acid (rosin)	23·00	32·45 „
Water	3·40	5·34 „
Soda	2·80	1·45 „
Sulphur	...	0·25 „
Chlorine	...	0·14 „

From the very interesting research of H. Collier[4] on the emulsive properties of rosin soap, we learn that soap manufactured by two hours' boiling of 112 g. rosin with 20 g. caustic soda and 580 g. water is able to convert even mercury, on shaking immediately into the state of finest division, and that oils, chloroform,

[1] *Pharm. Centralhalle*, 1884, p. 290. [2] *Ibid.*, 1889, p. 227.
[3] *Z. angew. Chem.*, 1891, p. 183.
[4] *Pharm. J. and Trans.*, 1890, xx., p. 751.

thymol, camphor spirit, creosote, etc. are quickly and completely emulsionated by adding a small quantity of rosin soap.

From the above analyses we see that the creoline analyzed by Otto & Beckurts was made with 30 parts of rosin, which was saponified and dissolved in 70 parts creosote oil; whilst the article analyzed by Sprenger was made from 40 parts rosin and 60 of creosote oil. This, as well as further analyses, prove that the "creoline" of trade has been very differently composed at different times; and this is still further proved by the existence of other creolines (such as Ortmann's Ger. P. 51515, 1889), in which the emulsion of creosote oil is effected by the addition of solutions of gum arabic, or of certain sulphonic acids of heavy hydrocarbons.

Quite a number of coal-tar preparations, sold for antiseptic purposes, go by the name of "creoline." Their value is very unequal, and properly speaking should be tested by their bactericidal action.

According to Baroni,[1] good creoline is a brownish-red, clear liquid, smelling of coal-tar, not unpleasantly, sp. gr. 1·03 to 1·08, yielding in the proportion of 1 : 40 a milk-white emulsion which keeps for weeks. Good creoline contains from 2·5 to 4·5 per cent. NaOH, partly saponified, and 70 to 80 per cent. coal-tar oil (a sample of Pearson's creoline showed 78 per cent.), as extracted by ether. The percentage of phenols is about 20 per cent. Creoline is prepared by saponifying the rosin with a solution of caustic soda, sp. gr. 1·332, at 100° C., adding the coal-tar oil, previously heated to 70° or 80°, mixing at 100° and filtering. Baroni gives the following quantities for various qualities of creoline:—

	Venetian turpentine.	NaOH solution, 1·332 spec. grav.	Coal-tar oil, spec. grav. 1·08 to 1·085	Colophonium rosin.	Beef suet.
	Grms.	Grms.	Grms.	Grms.	Grms.
1. Italian creoline . .	250	70	775	...	...
2. Ordinary creoline . .	...	90	780	200	...
3. Solid creoline, f.-p. 55° to 58°	70	90	750	60	80

The following table shows the composition of two com-

[1] *Giorn. Farm. Chim.*, li., 289.

mercial creolines of good quality, besides that of "Italian Creoline":—

	NaOH.			Coal-tar oil.	B.-p. of coal-tar oil. ° C.	Phenols and cresols.	Rosin.
	Not Saponified.	Saponified.	Total.				
Creoline A. .	1·76	0·96	2·72	77	180 to 270	12	17·5
Creoline B . .	2·96	0·32	3·28	66	170 „ 260	16	27·3
Italian Creoline	1·84	0·76	2·6	76	160 „ 270	16	19·0

In Germany the designation of "creoline" was officially restricted in 1903 to the "Creoline Pearson," *supra*, p. 629.

Alb. Friedländer (Ger. P. 181288) makes phenol or its substitution products soluble in water by adding small quantities of sulphonic acids or sulphonates.

Lysol is a preparation now extensively employed, because it is perfectly soluble in water. Such a preparation was first made by Schenkel and sold as "sapocarbol." Lysol itself, according to Dammann's patent[1] (Ger. P. 52129), is made by mixing tar oils, rich in phenols and cresols, with linseed oil or rosin and saponifying the oil or rosin by caustic-potash solutions and spirit of wine, heating with a reflux cooler until the mixture is homogeneous. Thus brown, oily, viscous, translucent liquids or semi-solids are obtained, easily soluble in pure water.

According to Gerlach,[2] lysol is made from the first portions of creosote oil, passing over between 199° and 201° C.; these contain mostly phenol and cresols, and scarcely any neutral oils.

Reuss[3] gives the following analyses of lysol:—

Constituents.	Brand "Eisenbüttel."	Brand "Schülke & Meyer."
Pure cresols . . .	49·20	44·58 per cent.
Impurities of crude cresol .	0·76	4·40 „
Potassium linoleate . .	19·80	27·83 „
Glycerin of soap . .	2·13	3·48 „
Glycerin added besides .	...	4·12 „
Water	21·34	9·32 „
Ashes	6·51	7·17 „

Lysol is employed like creoline (or carbolic acid), especially also for surgical operations. They both render the skin and

[1] Later on cancelled by a decision of the German Reichs-Gericht.

[2] *Chem. Zeit.*, 1890, p. 1289. [3] *Chem. Ind.*, 1897, p. 8.

the instruments slippery on washing, which is not the case with the "Cresol Raschig," to be described below.

Since a number of accidents have been caused by the use of lysol, and it has also been abused for criminal purposes, the German Federal Council, by order of February 1, 1906, has withdrawn it from free sale, so that it may be sold only when prescribed by a medical man.

Knoll & Co. (Ger. P. 166975), in order to purify heavy tar oil for therapeutic purposes and prevent their darkening in course of time, first remove the acid oils and bases, then wash them several times with 2 or 3 per cent. concentrated sulphuric acid with the assistance of oxidizing agents, wash again with alkali and redistil them at diminished pressure in stills where they do not come into contact with base metals.

A product obtained in this way is sold as "Anthrasol"; *cf.* Bokorny in *Chem. Zeit.*, 1904, 990.

Seyd's "Lysokresol" is described by Arnold and Mentzel (*Apoth. Zeit.*, xviii., p. 134; *Chem. Centr.*, 1903, i., 784). They give analyses, quoting the thousandth part of a milligram of cresols and neutral oils. Lysokresol evidently differs from real lysol only by containing more water and being made from impure cresol.

"Lysoform" is a compound of lysol and formaldehyde.

A similar compound is Rosemann's "Carbolic-acid soap" (B. P. 28277, 1902), made from water-white crude cresol, with 2 per cent. formaldehyde and 240 per cent. formaldehyde-potash soap (containing 15 per cent. COH). It is almost devoid of smell, easily soluble, not strongly poisonous, and very efficient.

"Lysosulfol" (*Pharm. Zeit.*, 1901, 92) is a sulphur compound of lysol, soluble in water.

"Carbollysoform" is a mixture of 2 parts lysoform with 1 crude carbolic acid.

The German Imperial Board of Health has published the following prescription for a 5-per-cent. solution of crude carbolic acid in soap: Dissolve 3 parts soft green soap in 100 parts hot water, and pour in 5 parts of crude (100-per-cent.) carbolic acid, with frequent stirring.

Cresol Raschig (*Z. angew. Chem.*, 1896, p. 358) is intended to obviate the drawback of lysol and creoline, viz. rendering the skin and instruments greasy. Raschig agitates 200 parts cresol

with 25 parts of 25-per-cent. caustic-soda solution, and adds 100 parts olein and 25 water. This mixture is easily soluble in water.

Hirschsohn (*Fischer's Jahresb.*, 1893, p. 540) renders cresol soluble by mixing 100 parts with a solution of 50 rosin and 6 or 8 sodium hydrate in 12 to 16 water. Hiscott (B. P. 20246, 1896) mixes 50 to 100 parts commercial carbolic acid with half its weight of melted rosin, sufficient concentrated caustic-soda solution, and 4 to 8 parts cotton-seed or cocoa-nut oil; or else $\frac{1}{2}$ to 2 parts α-naphthol to 100 soluble phenol.

Raupenstrauch (Ger. P. 178794) mixes the ordinary alkali-cresol soap with salts of heavy metals.

Carbolic-acid Soap is generally sold as containing 10 per cent. or even 20 per cent. of carbolic acid, but very often it contains much less (*cf.* Allen's analyses, p. 639), and in any case loses some of it in the course of time by evaporation. The cheaper descriptions contain mostly cresol; they can be made in the cold by kneading carbolic acid with curd soap and pressing into moulds, but preferably by melting the soap and mixing it with carbolic acid in the liquid state. Jeyes (B. P. 16427, 1885) saponifies a mixture of carbolic acid with cocoa-nut oil by caustic soda, and makes the product more soluble by adding sodium sulphate or carbonate during the fusion. Hargreaves (B. P. 18469, 1889) employs for this purpose the chlorinated phenols or their salts. Another British patent (*Chem. Ind.*, 1897, p. 346) prescribes mixing at 200° F. 95·76 parts of 77-per-cent. caustic potash with 250 carbolic acid or tar oils, 255 oleic acid, and so much water that a liquid soap of 12 per cent. strength is formed; or else the oleic acid is first saponified and the disinfectant and water are added afterwards.

Many publications have been made in 1907 on cresolic soaps, which are reported on by Fortmann in *Chemische Zeitschrift*, 1907, p. 118.

Carbolic-acid Preparations of Non-soapy Character.

Helmers (Ger. Ps. 76133 and 80260) renders phenols soluble by means of the sulphonic acid of mineral or rosin oil.

The Chemische Fabriks-Aktien-Gesellschaft in Hamburg (Ger. P. 72101) found that the syrupy solution of the sodium or potassium sulphonates of phenylxylylethane and its higher homologues (remaining behind in the purification of crude

xylol) dissolves tar oils and cresols, without leaving the solution liable to be decomposed by acids.

Lembach and Schleicher (Ger. P. 73117) prepare soluble crystallizable, non-poisonous disinfectants, called "oxychinaseptol" or "diaphtherin," by the action of 2 mol. ortho-oxyquinoline or its homologues on 1 mol. phenol or its homologues, 1 mol. sulphuric acid, and at least 3 mol. water. The new substance crystallizes in fine needles or large hexagonal prisms.

Ortho-oxyquinoline is also employed by Fritzsche (Ger. P. 88520). Two mols. of this substance are boiled ten or twelve hours in an alcoholic solution of 1 mol. sodium pyrosulphate till no further action takes place. The product, when cold, is separated from adhering alcohol, dried, and powdered. It is soluble in water, and the solutions dissolve phenols in every proportion, exempt from smell and irritating or poisonous properties, but strongly bactericidal. This "cresochin" contains 33 per cent. quinoline, and 17 per cent. cresols.

F. von Heyden's Nachfolger (Ger. P. 57842) make a solution of 12 parts sodium salicylate, 10 cold water, and 5 cresol, which can be diluted at will. Naphthol behaves in the same way. These preparations are sold as "solveol" for surgical purposes, and "solutol" for ordinary disinfection; they are easily soluble, of constant composition, and do not render the hands, etc., slippery. Hammerl (*Chem. Ind.*, 1891, p. 298) declares a ½ per cent. solveol solution to be more effective against bacteria than 2 to 5 per cent. carbolic-acid solution.

"Sozal" (Scherges, *Pharm. Zeit.*, 1892, p. 489) is aluminium paraphenolsulphonate; crystalline, easily soluble in water, glycerin, and alcohol, and more efficacious than aluminium acetate in the treatment of ulcers, etc.

The "sozoiodols" of Trommsdorf unite the action of iodoform with that of carbolic acid in the treatment of wounds. One of these is more soluble, viz. the diiodparaphenolsulphonate of sodium, $C_6H_2I_2 . OH . SO_3 . Na$; another, the acid potassium salt, is less soluble.

Nördlinger's "saprol" (Ger. P. 70578), a dark-brown liquid, contains 40 per cent. cresol, 40 per cent. heavy tar oils, and 20 per cent. petroleum hydrocarbons. It is not completely soluble, but floats on the sewage and gradually communicates to this its

disinfectant agents. It is well spoken of by Laser (*Centr. f. Bakteriol.*, 1892) and Scheurlen (*Arch. f. Hyg.*, 1893, p. 627), whilst according to Keiler (*ibid.*, xviii., p. 57) the soapy disinfectants are preferable.

"Phenosalyl" is a mixture of carbolic acid, salicylic acid, lactic acid, menthol, glycerin, and borax.

"Microsol" is a solution of cupric sulphate, containing free sulphuric acid and 10 per cent. cupric phenolsulphonate.

"Sanatolyse" consists of carbolic acid, sulphuric acid, and ferrous sulphate.

Gentsch (Ger. P. 156761) first prepares solutions of phenols in benzol, chloroform, CS_2, etc.; by mixing them with dry alkaline carbonates, hydrates, or phenolates, crystallized double compounds of phenol and potassium phenolate are obtained, thus:

$$K_2CO_3 + 4C_6H_5.OH = C_6H_5OK.3C_6H_5.OH + KHCO_3.$$

The double compound can be separated from the alkaline bicarbonate by hot benzol or alcohol; after filtering from the $KHCO_3$ and cooling, the solution deposits shining needles of that compound, fusing at 106° to 108° C. The corresponding paracresol compound, $C_6H_4(CH_3)(OK).3C_6H_4(CH_3)(OH)$, fuses at 147° and is easily separated from the more soluble ortho- and meta-compounds by fractional solution. A second patent of the same inventor (Ger. P. 157616) prescribes working without solvents. He introduces, *e.g.*, solid caustic potash into paracresol and heats until all is dissolved. On cooling the whole solidified to a yellow crystalline mass of the double compound, as formulated above.

The Farbenfabriken vormals Bayer & Co. have obtained the B. P. 9953, 1904, for this process. The compound prepared by them is sold by the name of "Metakalin," in the shape of tablets.

"Kresulfol Riedel" is a very cheap and efficient disinfecting mixture, made from 1 vol. crude cresol and ½ vol. commercial sulphuric acid. This mixture is applied in the shape of a 3-per-cent. aqueous solution.

Busse (*Chem. Zeit.*, 1885, p. 602) employs phenol-zinc solution for preserving timber from dry rot and decay. The solution is laid on with a brush, preferably after being mixed with magnesia.

"Odourless antinonnin carbolineum" is saponified ortho-dinitrocresol-potassium.

A paper by Seel in *Z. angew. Chem.*, 1906, p. 271, treats generally of the part played by the numerous class of old and new cresol preparations.

Obermüller (*Berl. Ber.*, 1907, p. 3623) has studied in detail the action of sulphuric acid on phenols.

Carbolic-acid Powders, etc.

Several advantages are attached to disinfectants in a solid state. They are more easily handled, with less inconvenience to the outside world by leakages, etc.; there is also less danger of their being abused as poisons, whether accidentally or purposely, since they are not as easily swallowed as liquids. A number of the preparations mentioned before is already in the solid or pasty state; here we treat those where the solid state has been purposely aimed at for this or that purpose.

Macdougal's Disinfecting Powder (*cf.* also p. 294) is a mixture of crude carbolic acid with impure calcium sulphite (made by passing sulphur dioxide over heated limestone).

Calvert's Carbolic-acid Powder is a mixture of carbolic acid with the siliceous residue from treating china-clay with sulphuric acid (in the manufacture of patent alum). It should contain from 12 to 15 per cent. of carbolic acid; but the percentage is often far below this; it is ascertained by distilling, say, 100 g. in a glass retort. The distillate is partly oily, partly aqueous. The oily portion should at least be tested with caustic-soda solution (p. 607), since it generally contains valueless indifferent tar oils. The phenol contained in the aqueous portion can be estimated by bromine-water. Disinfectants containing lime should be slightly acidified before distillation.

Messrs C. Calvert & Co. have manufactured also a 50-per-cent. preparation in tablets (*Chem. News*, xl., p. 38).

Süvern's Disinfecting Mass consists of lime, magnesium chloride, and tar, and only indirectly belongs to this class (Schroeder and Berens, *Dingl. polyt. J.*, cxxx., p. 134; *cf.* also *supra*, p. 294).

Ziurek (*Dingl. polyt. J.*, xxx., p. 134) prepares a disinfecting powder by slaking 100 parts of quicklime and adding 5 parts of carbolic acid, intimately mixing them. Köhler (*Z. angew. Chem.*,

1894, p. 515) adheres to this prescription for technical "carbolate of lime." The brown colour required in the trade is obtained by adding the carbolic acid to the slaked lime while still quite hot, which favours the formation of rosolic acid. But this, as Köhler observed, may lead to the mass taking fire and burning out.

Heydenreich and Beilstein (*Fischer's Jahresber.*, 1881, p. 976) as well as Pettenkofer (*Cholera Regulativ*, München, 1867) object to the application of caustic lime.

Carbolic-acid tablets, for deodorizing the air in water-closets, hospitals, etc., are made by soaking pasteboard (Homburg, *Wagner's Jahresber.*, 1880, p. 740; also Crace Calvert & Co., *cf.* above), gypsum (Reyhe & Söhne, Ger. P. 9094), or porous earthenware (Kubel, Ger. P. 9526) with carbolic acid.

Holtz's Phenolith (Ger. P. 6498) is made by dissolving anhydrous boric acid in phenol or cresol, which take up about 40 per cent.; the mass forms a stiff paste, and can be converted into a powder by adding a little common salt, borax, or saltpetre. Lutze (B. P. 22136, 1897) mixes in a similar way carbolic acid with anhydrous boric or arsenious acid, alumina, magnesia, calcined borax, alum, or phosphates, to obtain non-hygroscopic powders.

R. Rütgers (Ger. Ps. 137584 and 141421) makes preparations of phenols with anhydrous oxalic acid. Very similar is H. Schneider's Ger. P. 189960.

Dowson (B. P. 11908, 1895) gelatinizes phenols by adding a little beeswax, or carnauba-wax, paraffin, Chinese or palm-wax.

England (B. P. 16422, 1894) makes antiseptic manure by mixing antiseptic tar-products with superphosphates, if necessary with addition of gypsum.

"Lysopast" and "Phenopast" are mixtures of lysol and phenol of the consistence of a salve or paste.

Raetz (B. P. 27889, 1903) renders solutions of phenol- or cresol-soaps solid, to increase their action by treating them at high pressure with aldehydes or ketones.

Analysis of Carbolic-acid Preparations.

Two processes must be distinguished here: the estimation of phenol in the presence of soaps (creoline, lysol, carbolic soap), and the estimation of the efficiency of a disinfecting powder. All other cases can be treated by one of the previously described methods.

Allen[1] recommends the following process for *determining phenols in "carbolic soap"*:—Five grams weight of the sample are dissolved in warm water, with addition of from 20 to 30 c.c. of a 10-per-cent. solution of caustic soda. The cooled solution is then agitated with ether, and the ethereal layer separated and evaporated at a low temperature. The weight of the residue gives the amount of hydrocarbons, etc. The alkaline liquid separated from the ether is then treated in a capacious separator with an excess of strong brine, which completely precipitates the fatty acids as sodium salts. The liquid is well agitated, and then passed through a filter. In cases where the soap does not readily coagulate, an addition of a small quantity of tallow or palm-oil soap, previously dissolved in water, will usually overcome the difficulty. The precipitated soap is washed twice with strong brine, the washings being filtered and added to the main solution, which is then diluted to 1 litre. One hundred c.c. of this solution (= 0·5 g. of the sample of soap) are then placed in a globular separator, and acidulated with dilute sulphuric acid, when it should remain perfectly clear. Standard bromine-water is then added from a burette, the stopper of the burette inserted, and the contents of the burette shaken vigorously. More bromine-water is then added in the same way, until the liquid acquires a faint but permanent yellow tint. If crystallized carbolic acid has been employed for making the soap, the bromine derivative is precipitated in snow-white crystalline flakes, which allow the faintest yellow tint due to excess of bromine to be readily observed. If cresylic acid be the chief phenol present, as in the case of soaps made with Calvert's "No. 5 carbolic acid," the precipitate is milky, and does not separate well from the liquid, but the end of the reaction can still be observed. The addition of a solution containing a known amount of crystallized phenol is a useful device in many cases, as the precipitate then curdles readily, and the yellow coloration can be easily seen.

The bromine solution is made by mixing one measure of saturated bromine-water with two measures of water. This solution is approximately of 1 per cent. strength, and should be run out of a closely-covered Mohr's burette [no doubt a burette with glass tap would be preferable]. The last few cubic centi-

[1] *Analyst*, 1886, p. 103.

metres of the solution contained in the burette should never be employed. The bromine-water must be standardized immediately before or after use by a solution of Calvert's No. 2 or No. 5 carbolic acid, according to the kind of acid the titration has indicated to be present in the soap. This solution is made by dissolving 0·5 g. of the phenol in 20 c.c. of a 10-per-cent. solution of caustic soda, together with 5 g. of a non-carbolic soap. The solution is then precipitated with brine in the same manner as the sample, the filtrate diluted to 1 litre, and 100 c.c. acidulated and titrated with the bromine solution used for the sample. The volume of bromine solution used is that required by 0·050 g. of coal-tar acid of approximately the same quality as that contained in the soap.

The remaining portion of the liquid filtered from the precipitate of soap is best used for isolating the bromo-derivatives. It is acidulated with dilute sulphuric acid, and bromine-water added in slight excess. From 5 to 10 c.c. of carbon disulphide is then added, the liquid well agitated, and the carbon disulphide tapped off into a small beaker. The aqueous liquid is agitated with fresh quantities of CS_2 (of 5 c.c. each), till it no longer acquires a red or yellow colour. The carbon disulphide is then allowed to evaporate spontaneously, when a residue is obtained, consisting of the brominated derivatives of the phenols present in the soap. If crystallized carbolic acid of fairly good quality was introduced into the soap, the bromo-derivative is obtained in fine long needles having very little colour; and if all heating was avoided during the evaporation of the CS_2, the weight of the residue multiplied by 0·281 gives a fair approximation to the amount of carbolic acid. But if a crude liquid article has been employed, consisting mainly of cresol (cresylic acid), *e.g.*, Calvert's "No. 5 carbolic acid," the bromo-derivative will be deep yellow, orange, or red, with little or no tendency to crystallize, and the weight will not afford even a rough indication of the amount of coal-tar acid present.

By testing in this way, Allen found great deviations from the quantities of carbolic acid stated to be present by the manufacturers, *e.g.*, only 3·6 and 3·7 per cent. of phenol in "Carbolic Toilet Soap, ten per cent."

"Creolines" are analyzed by Weyl[1] as follows:—10 g. are

[1] *Berl. Ber.*, 1889, p. 138

extracted with 200 c.c. water, strongly acidulated with dilute sulphuric acid, well agitated, extracted with ether, and this extract treated with caustic-soda solution. The alkaline solution is repeatedly treated with small quantities of ether, and the extracts added to the principal portion. The total extract, containing all the *hydrocarbons*, is dehydrated by calcium chloride, filtered, cautiously freed from ether, left for twenty-four hours over sulphuric acid, and weighed. The alkaline solution is acidulated, treated with ether, and the ether treated with sodium-carbonate solution to extract the *acids*. The soda solution is acidulated with sulphuric acid and extracted with ether. The dehydrated ethereal extract is dried over sulphuric acid and weighed. The ethereal extract remaining after taking out the acids with sodium carbonate contains the *phenols*. It is dehydrated, cautiously evaporated, left twenty-four hours over sulphuric acid, and weighed. Soda is estimated by carbonizing about 3 g. in a platinum dish, evaporating with sulphuric acid, treating with ammonium carbonate, and igniting till the weight is constant.

We also refer to the methods described by Beckurts & Otto (*Pharm. Centralh.*, 1889, p. 227), Bodländer (*Reichs-Mediz. Anz.*, 1888, Nos. 10 and 11), Pfrenger (*Arch. Pharm.*, 1890, p. 701), Helbing & Passmore (*Pharm. Centralh.*, 1892, p. 507), Engler & Dieckhoff (*Arch. Pharm.*, 1892, p. 507), Reuss (*Pharm. Zeit.*, 1894, No. 60), Spalteholz (*Chem. Zeit.*, 1898, p. 58); Fresenius & Makin (*Z. anal. Chem.*, 1896, p. 325).

An elaborate paper by Ditz & Clauser (*Chem. Zeit.*, 1898, p. 733) describes the separation of fatty acids and phenols, *e.g.* in lysol. They saponify the whole with 10-per-cent. caustic-soda solution, extract the hydrocarbons from the solution with ether (afterwards evaporating the ether and drying over sulphuric acid), neutralize the remaining aqueous liquid with HCl, and add an excess of barium chloride, as well as sufficient barium hydrate solution for neutralizing the cresols. The barium oleate must be thus precipitated in the cold; it is quickly filtered, washed first cold, then hot, rinsed into a beaker, decomposed by HCl, and the fatty acids weighed as usual. The cresols contained in the filtrate from the barium oleate might be extracted by ether and weighed; but more exact results are obtained as follows:—The filtrate is acidulated, brought to a

known volume, and portions of this are titrated by Koppeschaar's bromine method (p. 619). Thus in the first instance the total bromine, a, is ascertained, which corresponds to all the phenols, which, however, absorb different quantities of bromine (p. 619). In order to ascertain the quantity of phenols, we must extract a certain (indefinite) portion of the acidulated solution by ether, evaporate the solvent, dry and weigh the residue $= g$. This phenol residue is now dissolved in caustic soda or baryta, and titrated by Koppeschaar's method; the bromine absorbed $= b$. If c is the original weight of lysol, the percentage of phenols is

$$\frac{100 \times a \times g.}{b \times c}$$

Spalteholz (*Chem. Zeit.*, 1909, p. 181) tests carbolic acid soaps merely by an approximate estimation of their percentage of water, by means of titration with acetic acid until a permanent opacity is produced.

Disinfecting powders are more simply analyzed by distilling 100 g. (if containing lime, after adding sulphuric acid) in a glass retort and separating the oily and watery distillate. The former often contains a great deal of worthless tar oils, and must be at least tested with caustic-soda solution (p. 607); the aqueous portion contains phenols, and must be tested by the bromine method.

Further papers on the examination of carbolic acid disinfectants are by Williams (*J. Soc. Chem. Ind.*, 1888, p. 826), Muter & de Koninck (*Analyst*, 1887, p. 191), Stavely (*Chem. Zeit.*, 1889, p. 1126; extract, *J. Soc. Chem. Ind.*, 1889, p. 1012), and Swoboda (*Chem. Zeit.*, 1891, p. 1041). We can here only mention these; the originals must be referred to for full particulars.

A process worked out by Clessler consists in shaking 10 c.c. of the liquor in a graduated test-tube with 6 c.c. official hydrochloric acid and heating in the water-bath up to the complete separation of the oily layer. After washing down to 15°, the volume of the latter is read off. This process has met with several objections. Schmatolla,[1] describes a similar process. He puts into a 200 c.c. cylinder 50 c.c. dilute sulphuric acid,

[1] *Chem. Centr.*, 1904, ii., 1518.

adds 100 g. (weighed) of the cresol-soap solution, shakes up and allows to settle for an hour. At least 73 c.c. of cresolic oil should be separated, sp. gr. at 15° at least 1·004 after filtration, corresponding to 67 per cent. cresol in the oil or 49 per cent. in the liquor. For each degree C. over 15° 0·0006 is to be deducted off the specific gravity.

The newest prescription (1904) of the German Board of Health for the testing of Liquor Cresoli saponatus is this: acidulate with sulphuric acid, distil by means of steam, shake the distillate with ether, evaporate the ethereal solution and dry the cresols thus obtained. This prescription holds good also for testing any other preparations containing no neutral oils such as lysol. The "drying" of the cresols, as pointed out by Russig, should not be performed by the application of anhydrous sodium or potassium carbonate, since these will take up some cresol, as proved by the compound found by Gentsch (p. 635) and by Russig in testing benzolic solutions of phenols.

The Society of Swiss Analytical Chemists (*Chem. Zeit.*, 1907, 1028) demands the following prescriptions to be fulfilled by cresol-preparations intended for disinfecting purposes, and as remedies against vegetable diseases. 1. They must be perfectly clear and soluble in water, alcohol, ether, petroleum, benzin, benzol, chloroform and glycerin. 2. They must contain at least 50 per cent. phenols and cresols, boiling between 187° and 210°, as proved by distilling 100 c.c. in a 300 c.c. flask, in which the thermometer bulb goes down 10 mm. below the side tube, then adding a little common salt to the distillate, when there must be at least 45 c.c. of cresols separated out. 3. Cresol preparations for medical and veterinary purposes must have a neutral reaction against phenolphthalein, when shaken up with five times their bulk of salt solution and filtering off the the solution.

Napthalene.

Naphthalene is always contained in coal-gas, and as it gives rise to troublesome crystallizations in the gas pipes, a number of processes has been devised for taking it out of the gas; but this does not belong to our present task, no more than the recovery of naphthalene from natural mineral oils.

Naphthalene is one of the most abundant constituents of

coal-tar. Its proportion is rarely below 5 per cent., and it may amount to perhaps 10 per cent. of the weight of the tar. Large quantities of it are obtained in the crude state, mostly unintentionally, by the cooling down of creosote oil; the first portions of this sometimes solidify almost entirely. This crude naphthalene was formerly considered a nuisance, as the buyers of creosote oil objected to it, and there was no outlet for it. Even now nothing like the whole of the naphthalene contained in coal-tar can be utilized otherwise than as an admixture to creosote oil or as fuel; but there is already a considerable demand for colour-making and for carburetting gas (see end of this chapter), and much naphthalene is therefore now taken out of the creosote oil for this purpose.

Livesey and Kidd (Amer. P. 258778) propose doing this more efficiently by heating "dead oil" in a closed boiler, and passing a current of air over the surface of the liquid. The air carries off the naphthalene and a little oil, which are condensed in a chamber. The condensed mass is immediately utilized for the manufacture of an article suitable for carburetting air or gas, by reheating it and casting it in cold-water jacketed moulds, like candle-moulds, but wider at the top. The sticks are taken out of the moulds the moment they are set, and the oil (which floats on the surface) is wiped off before it can sink into the naphthalene. The oil would not separate without the water-jacket.

This process can at the best only yield a very badly refined sort of naphthalene. In Europe, at any rate, only such naphthalene is now saleable which does not readily turn pink on exposure to the air; and this can only be made by more careful treatment, including hot-pressing, chemical washing, and distilling.

Refining the Crude Naphthalene.

The *hot-pressing* of crude naphthalene is perhaps the most important process for refining it; some even assert that it can be so conducted as to dispense with chemical washing before distilling the naphthalene. This process is conducted in presses with hollow plates heated by steam, like stearin-presses, or the presses used in the refining of anthracene (*cf.* pp. 476 *et seq.*) employing pressures up to 300 atm. Of course

very much depends upon properly regulating the temperature. The higher this is kept, the more complete will be the removal of the impurities; but then a good deal of the naphthalene itself will be removed as well, long before its own melting-point is attained, as its solubility in the accompanying oils increases rapidly with a higher temperature.

The operation of separating the naphthalene from the impurities may also be effected by heating the impure mass to a certain temperature and then subjecting it to pressing or centrifugal action; but this is less efficient than the treatment in a steam-heated press (*cf.* Anthracene, p. 480).

The processes for refining naphthalene have now been improved so far that a perfectly pure article can be made at a comparatively very low cost from the crude naphthalene crystallizing out of creosote oil, and some workmen even prefer this to the naphthalene from carbolic acid; but at other tar-works pure naphthalene is exclusively obtained from the just-mentioned source.

This naphthalene is made from the same oil that serves for preparing phenol, viz., from the residual oil remaining after the alkaline treatment. This is decidedly rational, as thus one of the expensive purifying agents is utilized beforehand for another purpose. Indeed, when the oils drawn off from sodium carbolate are distilled in the light-oil still (see next chapter), at first a little light oil passes over, but afterwards almost pure naphthalene. This is seen on mixing a sample of the distillate with cold water, when no more oil collects on the top, but white crystallized masses float all over the water. The receiver is now changed, and the distillation is continued with the precautions to be described below for preventing any choking-up. The receiver contains, a white crystallized magma, from which, after cooling, the naphthalene is separated by pressing. This ought to be done in a *hot* press.

Most of the naphthalene certainly separates out when the carbolic acid cools down. At all events all the crude naphthalene, both from the crude oils and from redistilled (but not yet washed) oils, is treated together.

First of all the oily portions must be removed. This can be done roughly by draining on a perforated bottom or a cemented floor. The naphthalene then still contains from

10 to 16 per cent. of oils. These can be to a great extent removed on centrifugals, all the better on account of the coarsely crystalline structure of naphthalene, or else by cold hydraulic pressing in sacks at a pressure of 200 atmospheres. At a large English works, instead of this they at once distil the drained naphthalene, keeping out the first 10 per cent. of the distillate, collecting the next 70 per cent., and rejecting the remainder. The 70 per cent. just mentioned is kept in casks for a week in a cool place; then the inner, oily core is removed, and the hard, outer crust is allowed to lie on an inclined floor for another week for the last portions of oil to drain off.

At another large works they distil the cold-pressed naphthalene, keeping out 8 or 10 per cent. as first runnings and collecting the next 80 per cent. These are then hot-pressed at 200 atmospheres. This is done by putting the naphthalene into bags, holding from 35 to 40 lbs. each, placing them in water of 75° C., and then arranging 20 or 30 such bags in the press, where they remain for 2 or $2\frac{1}{2}$ hours. The hard cakes are trimmed all round with a sharp tool; the oily outer portions are once more pressed, and the inner portion goes to the washing process.

Distillation of Naphthalene.—The stills are shallow wrought-iron vessels, holding a ton or upwards, heated by a direct fire, but protected against its first action by a curtain-arch; they are provided with a manhole, a safety-valve, and a very high head (up to 7 feet), which can be furnished with contrivances for dephlegmation, but which already acts in this direction by the cooling effect of the air.

The condensation is effected by a simple iron worm similar to those used for tar, but with the water in the tub always kept at 80° at least; sharp elbows and the like (where at the end of the operation solid naphthalene might accumulate and cause in the next operation a dangerous tension in the still, or ultimately an explosion) should be avoided. If after all a plug of naphthalene should choke up the worm without its presence being at once detected (in which case it could be melted by boiling-water), the safety-valve will blow out. This is a signal for instantly drawing the fire; in the worst case the still must be cooled from above by pouring water upon it.

All danger of choking up is avoided, when distilling in a

vacuum, by employing an air-tight receiver and exhausting the air by means of a pump; and we would greatly recommend this method of distilling naphthalene for other reasons as well.

In lieu of an ordinary safety-valve (which easily gets fixed and anyhow might not act quickly enough) a contrivance like that shown in Fig. 161 is sometimes employed. Upon the still is fixed a flanged pipe, *a*, 12 inches wide, covered by a metal plate, *b*. Hemp packing and the weight of *b* suffice for keeping the joint tight without screwing down the arm *c*. The latter is quite loose, and its only object is to prevent the cover *b* from being violently jerked away whenever it is lifted by excessive tension in the still; the cover will then be lifted as far as *c* allows it, and will permit the vapours to escape.

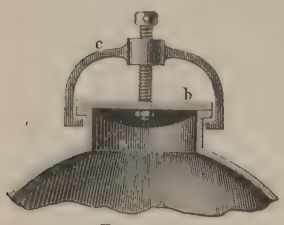


FIG. 161.

Watson Smith (*J. Soc. Chem. Ind.*, 1882, p. 343) thinks it safer and simpler to have a small hole bored in the still-top and closed by a cork, which, if there is too much pressure, would be blown out with some force. For large stills the outlet thus gained for the vapours would be hardly sufficient. Compare also what has been said respecting tar-stills, pp. 337 and 366.

Some manufacturers, in order to avoid any danger of choking-up, work without a worm, with an apparatus similar to that shown in Fig. 162. The vapours pass through the tube *a*, kept warm by the steam-pipe *b b*, into the wrought-iron cylinder *d*. Opposite *a*, running in the same slanting direction, is a pipe, *c*, through which the steam-pipe *b* comes out. Thus *a* is prevented from being choked up, and *c* also serves for an occasional cleaning-out. *d* is placed to two-thirds of its height in a wider cylinder, *f*. If the cooling effected by the outer air is not sufficient, water is run upon *d*, which collects in the outer cylinder and runs away. But the temperature in *d* is kept high enough for the naphthalene to remain liquid and to run out through the pipe *e*. It is collected in shallow iron dishes, where it solidifies into cakes, which are either broken up and packed at once, or again subjected to hydraulic pressure.

In distilling, first of all a little water and light oil appears.

When the thermometer (in the vapour) has risen to 210°, the receiver is changed and pure naphthalene collected up to about 230°. Then either the still is stopped and the residue run to the creosote oil, or the distillation is continued into another receiver, and the impure naphthalene collecting there is again purified. Apart from the danger of choking-up, the distillation is easy and quick.

Mateu (B. P. 25989, 1903) proposes purifying naphthalene, without chemical treatment, by distilling or subliming it in a current of air, making use of the difference in volatilization and condensation between naphthalene and the impurities.

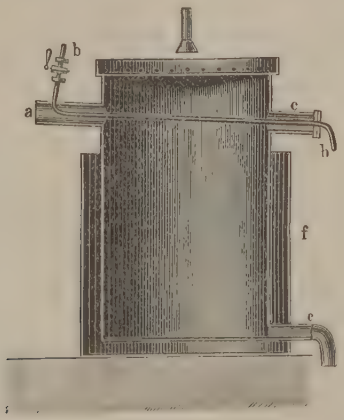


FIG. 162.

(It is hardly likely that by this process a quality sufficient for the manufacture of colouring matters will be attained.)

Now follows the *chemical washing*. If the oils have not been previously submitted to an alkaline treatment, the washings must begin with this. The caustic liquor may be of any convenient strength. The treatment is effected in closed iron vessels, heated above the fusing-point of naphthalene (79°) by a steam-jacket or a coil, and preferably provided with a mechanical agitator. With very impure naphthalene this treatment should be repeated. In any case the fused naphthalene must be mixed up for some time with the liquor, and after the latter (which collects at the bottom) has been run

off, the naphthalene should be washed with hot water, which will now rise to the top.

With better crude naphthalene, especially that distilled in the manner mentioned above from carbolic-oil residues, the alkaline treatment may be dispensed with, and the washing begun with sulphuric acid, which in the concentrated state removes the residual phenols in the shape of sulphonic acids. Vohl[1] recommends sulphuric acid of 45° Baumé (= sp. gr. 1·453). According to my experience this is too weak; acid of at least 1·740 sp. gr. should be employed. The strongest vitriol, of sp. gr. 1·84, is even better; but at that temperature it dissolves much naphthalene, so that less, though of a better kind, is obtained. At some works they wash first with dilute and then with strong sulphuric acid. On the large scale about 5 per cent. of acid will suffice; sometimes 3 per cent. is sufficient.

The mixture with sulphuric acid is effected in wooden or iron vessels lined with lead, or best of all in cast-iron cylinders, heated by indirect steam and provided with an agitator: the subliming of naphthalene during this operation is rather troublesome. Now follows washing several times with water and then with weak alkaline liquor, to remove all acid, and finally distillation (see below).

The washing of naphthalene, both with acid and alkali, is preferably performed in steam-jacketed vessels provided with a horizontal agitating-shaft.

Before distillation, some manufactures employ an oxidizing treatment in order to avoid a subsequent reddening of the naphthalene.[2] At an English works they add to the melted naphthalene 1 per cent. potassium bichromate and the necessary quantity of sulphuric acid, sp. gr. 1·7, agitate for two hours, add a little water, agitate another half-hour, allow to settle for two hours, and draw off the green liquid at the bottom. Following this comes the washing with sulphuric acid, sp. gr. 1·84, then with dilute water, and at last with pure water to which enough sulphate of soda is added to render the specific gravity sensibly greater than that of the fused naphthalene.

I have (see *Berl. Ber.*, 1881, p. 1755; *Chem. News*, xliv., pp.

[1] *J. prakt. Chemie.*, cii., p. 29.

[2] Dr Kraemer (priv. comm.) considers this superfluous.

65 and 142) succeeded in thoroughly purifying naphthalene by treating it with a few per cent. of "Weldon mud" (recovered manganese dioxide, or rather calcium manganate) and sulphuric acid of sp. gr. 1·7 or 1·84. Even ordinary, ground manganese ore can be employed for this purpose, by mixing 5 per cent. of it with melted naphthalene, adding 10 per cent. sulphuric acid, gradually or in two portions, and stirring for half an hour or an hour.

Naphthalene from washed carbolic oil requires no alkaline treatment. At the present low prices of naphthalene most manufacturers employ only sulphuric acid and very little caustic-soda solution.

The *second distillation* of naphthalene is sometimes, but not usually, performed in a still provided with a "column" head, to obtain an absolutely uniform product (*cf.* p. 645).

When redistilling the washed naphthalene, there is a small quantity of aqueous first runnings. After this follow 80 per cent. of pure naphthalene, which can be directly run into casks lined with sized paper and allowed to solidify. The distillation is continued so long as a sample solidified on a watch-glass and covered with pure sulphuric acid (1·84) does not stain this yellow and dissolves therein on heating with at most a faint brown colour. As the by-products are always worked up again, the yield of pure naphthalene is about 70 per cent.

The distilled naphthalene is always run out of the condenser in a liquid form, and is usually run upon a large metal plate or shallow pan, where it solidifies, and is then broken up into small pieces, and sometimes ground into powder. Special smaller moulds are occasionally employed. The naphthalene required for the albo-carbon light (see below) is cast into sticks, like those of refined sulphur ("brimstone in rolls"). This is done by means of hardwood moulds, with a little taper to facilitate the getting out, or by a moulding-machine such as is used at candle-works. A special machine for this purpose is that of Neujean (Ger. P. 36708).

Where large quantities of pure naphthalene are made, the *vapours* arising from the liquid naphthalene in the moulds, previous to its solidification, may cause an appreciable nuisance. This is prevented by providing the pan, serving as a mould, with a hydraulic lute, and fitting it with a cover suspended from

a crane, so that it can be removed after the naphthalene has cooled down, in order to clear the mould. This apparatus resembles the oxide-of-iron purifiers of gas-works.

The following processes for refining naphthalene are not extensively employed:—

G. Link (Ger. P. 35168) presses crude naphthalene repeatedly in hydraulic presses, distils it, and treats the distillate in a cast-iron agitator, similar to those used for manufacturing nitro-benzol, with a solution of soap at about 85°. Most of the mass enters into solution; the mixture is run into wooden tanks, is cooled down to 50° by cold water, dehydrated in a centrifugal machine, washed and distilled. The naphthalene now passes over almost chemically pure, as a limpid liquid, which solidifies to a large-flaked, snowy-white, crystalline mass. The impurities of crude naphthalene remain dissolved in the mother-liquor.

Dehnst (Ger. P. 47364) treats naphthalene with ½ or 1 per cent. brimstone at 170° or 175°. The impurities he states to be changed thereby into high-boiling substances, whilst the naphthalene is not affected.

Stenhouse and Grove (*Berl. Ber.*, 1876, p. 683) heat the otherwise purified naphthalene with a small percentage of sulphuric acid to a temperature of 180°, distil the resulting black mass in a current of steam, and repeat this process till the product dissolves at 100° in an excess of concentrated sulphuric acid without any colour. This process, employed by them for scientific purposes, would hardly pay on the large scale, and it would be very troublesome to sublime the naphthalene mixed with acid.

From Dr. H. Köhler I have received the following more recent communications on the manner in which he prepares technically pure naphthalene for the manufacture of naphthol and naphthylamine. The crude naphthalene, as it is obtained from cresote oil, etc., is allowed to drain on a plate with fluted surface, having been reduced to pieces of the size of a walnut or a hen's egg, in a layer of from four to five feet deep. After this draining it is submitted to cold hydraulic pressure at 200 atmospheres, and is then distilled in the still for crude naphthalene, above described. The distillate up to about 210° C. is received as "first runnings," and kept separate from the main distillate, coming over between 210° and 228°. The

latter is run into a receiver, heated by a steam-coil, and from this into shallow cast-iron moulds, where it very quickly forms cakes, about 2 ins. thick. These are wrapped in sheets made of coarse hemp cloth and placed in frames which give them an exact shape. The parcels thus formed are placed between perforated iron plates and built up with these in the hot press, where a wrought-iron grid is placed between each parcel and the heating-plates, so that the oil produced on pressing can run away. When the press is full, its temperature is raised to 70° or 75° by means of steam, and the pump is started. The pressure is *slowly* raised to 200 atmospheres; this pressure is maintained for some time, until no more oil runs off. Usually one pressing is sufficient; but some descriptions of naphthalene require a second pressing, as manifested by the oily appearance of the margins of the cakes. In this case the cakes are broken up, repacked as above described, and pressed over again.

Now comes the chemical treatment. The pressed naphthalene is melted in an apparatus provided with a mechanical stirrer, and is treated with sulphuric acid at a temperature not exceeding 100° C.; employing first about 2·5 per cent. of its weight of acid of sp. gr. 1·84, for the purpose of dehydration, and thereupon 5 to 7·5 per cent. by weight of acid, sp. gr. 1·70, the quantity varying according to the quality of the crude naphthalene. After running off the acid, or, preferably, forcing the naphthalene through a heated pipe into a second washing-apparatus, it is repeatedly washed with hot water, as described above.

The purified naphthalene, while still liquid, is forced into a still; here it is mixed with 5 per cent. of its weight of caustic-soda solution, sp. gr. 1·38, and after being separated from the salts is distilled as described on pp. 645 *et seq.*, observing the thermometer and taking samples from time to time. The first runnings of both distillations are worked up as previously described. The last runnings from the second distillation may be worked up for naphthalene in bars or balls.

Distilled pure naphthalene is mostly employed for the manufacture of naphthols, naphthylamine, phthalic acid, etc. For medicinal purposes and as an insecticide (against moths, etc.), it is preferable used in the shape of scales or powder. This can

be produced either by recrystallizing pure distilled naphthalene or by sublimation.

For recrystallizing naphthalene the ordinary solvent is

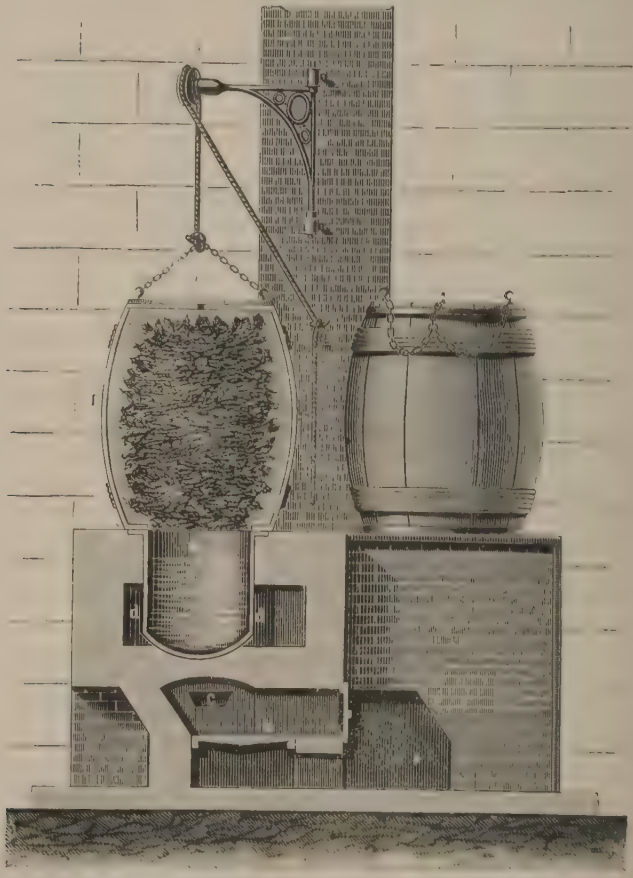


FIG. 163.

petroleum spirit. It is done in enamelled iron vessels provided with reflux coolers and heated by steam. The solution is either allowed to cool directly in these vessels, or else in other vessels provided at the bottom with a tap for drawing off the

mother-liquor. The crystals are centrifugalled and dried in the air. The coarser the crystals, the more are they favoured in trade; they are also more easily freed from solvent.

At some places amylic alcohol is used for recrystallizing naphthalene, in which case hardly any solvent is lost by volatilization.

The *subliming* of naphthalene does not require a distilled article to start with; it suffices to employ the naphthalene after treating it with sulphuric acid and alkali. The subliming can be done on a moderate scale in the apparatus Fig. 163 (taken from Wurtz). *a* is a pan for melting the naphthalene, heated by the fire on the grate *b*; *c* is the snore-hole; *d d* are flues.

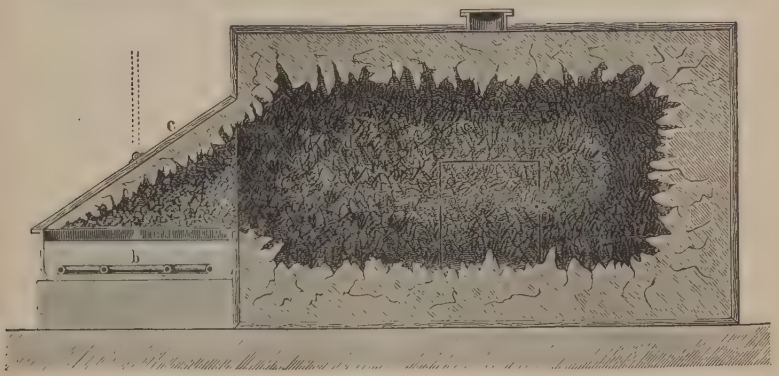


Fig. 164.

The pan is covered by a tub, *f*, suspended by chains from a small crane, *e*; in its top there is a small air-vent. The naphthalene sublimes into the tub, forms crusts on the sides, and is knocked out at the end, after moving the tub sideways. The fire should not be strong enough to cause the naphthalene to melt in the tub and run back into the pan.

The apparatus, Fig. 164, is intended for a larger scale of working. *a* is a shallow iron pan, say 10 ft. × 7 ft. × 3 ft. deep. The steam-coil *b* on its bottom serves for heating. The pan is covered by the slanting wooden roof *c*, whose lower part can be turned back into the position shown by the dotted lines. To this is attached a wooden chamber, *d*, say 16 × 10 × 5 ft.

with a working door, *e*, and a flap on the top, serving as safety-valve. The heat of the "dry" steam in the coil *b* suffices for subliming the naphthalene; it should not go so far as to give rise to distillation. The naphthalene collecting in *d* is taken out at intervals of a few days.

Sometimes steam blown into the mass ("wet steam") is preferred to dry steam. In this case there should be a compartment between the pan and the subliming-chamber, in which the condensed steam-water and a little melted naphthalene may collect.

The following apparatus for subliming naphthalene is described by Hirsch (*Chem. Zeit.*, 1884, p. 839):—Chamber A (Fig. 165) is made of 12-inch brickwork, standing isolated, 16 ft.

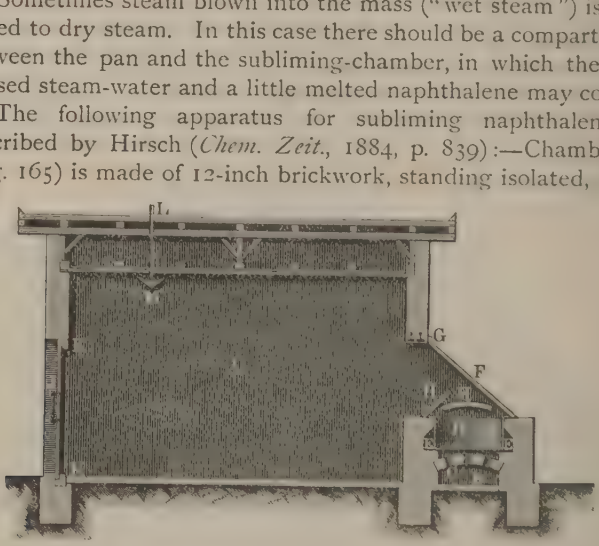


FIG. 165.

long, 10 ft. wide, and 10 ft. high. On the brickwork rests a light roof frame, covered with roofing-felt. B is a wrought-iron pan, 10 ft. long, 3 ft. 3 ins. wide, 19 ins. deep, set over the curtain-arch C in such way that the fire-gases from the hearth D first travel towards the back, then rise in the flues E round pan B and then escape in the chimney, which need project only 3 ft. over the roof. In the flue E there is a damper for regulating the draught. F is a wooden charging-door, covered with sheet-iron on both sides, turning round the hinge G; during the sublimation this door is luted with clay. H H are two wood covers, covered with sheet-iron, loosely lying on iron stays fixed on the side walls; they act as dephlegmators, condensing the heavy oils whose vapours are carried along by the naphthalene vapours. J is an iron-covered door, luted with

clay, for discharging the sublimed naphthalene. L is an iron air-pipe, 3 ins. wide, projecting inside 4 ins. and 18 ins. above the roof; it carries the dish M, in which is collected the water condensing in L.

Some manufacturers state that it is better to mix the naphthalene with sand before subliming; but this seems quite unnecessary.

It has also been attempted to effect the sublimation by blowing in hot air by means of a fan-blast; but this has been discontinued. Ordinary air easily produces a fire; and a previous removal of the oxygen by passing the air through a coal-fire is too expensive. Moreover, the condensation is more difficult than when the heating is produced by indirect steam.

According to Tammann (Ger. P. 95579), naphthalene and its homologues can be recovered from the acid-tar of refining petroleum. This process can never be advantageously employed for naphthalene itself, but may do perhaps for the di- and trimethyl-naphthalenes.

Examination of and for Naphthalene.

The properties of pure naphthalene have been described, p. 190. Commercial naphthalene is now required to be as chemically pure as possible. It should volatilize without any residue, fuse at 79·6° to 79·8°, and boil at 217° to 218°, under a pressure of 760 mm. In order to see at once whether a sample of naphthalene will turn pink or not, tests are made with sulphuric and nitric acids. On dissolving the sample in pure hot concentrated sulphuric acid, the latter should only turn faintly purple or pink: I have never yet met with a sample which left the acid entirely colourless, when dissolved in somewhat large quantity. Even the best commercial brands sometimes turn the acid pretty strongly red. The other test is made by pouring pure, *not* fuming, nitric acid on the bottom of a desiccator and placing the naphthalene in a watch-glass above it, covering up the whole as usual. If the sample remains white for half an hour it is good, and if for two hours it is excellent. Inferior descriptions soon turn pink. After some hours all samples turn yellow, probably owing to the formation of nitronaphthalene.

The presence of phenols in naphthalene is discovered by boiling the sample with a dilute solution of caustic soda, cooling, filtering, and adding to the filtrate bromine-water and hydrochloric acid; any phenols present will now be precipitated as brominated compounds.

Quinoline bases are discovered by dissolving the samples in concentrated sulphuric acid, pouring the solution into water, filtering, making the filtrate alkaline, and distilling, when the quinoline bases will pass over with the aqueous vapour, and will be recognised by their peculiar smell.

Häussermann (private communication to the author) points out that even a most thorough washing with acid and alkali does not free the naphthalene from certain other hydrocarbons which do not affect either the boiling-point or the other outward properties of naphthalene, but which make themselves felt in the subsequent manufacture of naphthylamine, naphthol, etc. These impurities are said to be removable only by certain solvents; but it would appear as if the hot-pressing of the naphthalene crystals, as it is now pursued at most works, equally tends to remove them.

The *examination for naphthalene* in commercial articles is nearly always based on its subliming property. Sometimes the acidimetric estimation described by Küster (*Berl. Ber.*, 1894, p. 1101) may be useful. It is based on the property of naphthalene to form an insoluble molecular compound with saturated solution of picric acid, the excess of which can be found by titration with lacmoid. The sample is placed in a small, strong flask, together with saturated picric-acid solution which fills it nearly to the neck. It is fitted with an indiarubber cork, through which passes a 7 cm. wide glass tube, closed at the bottom, but with a small lateral hole about 1½ cm. above the bottom. At first the tube is pushed down until the hole is free; the flask is evacuated by an air-pump, and the tube is then pulled up until the lateral hole is well within the cork. The flask is now heated on the water-bath until the reaction is complete; no naphthalene can escape during this time. After cooling over-night the tube is lowered to admit the air; the contents are filtered, and the picric acid in excess is titrated with barium hydrate. This process would also indicate acenaphthene, chrysene, and both naphthols, but not phenan-

threne; it is therefore only applicable where the former substances are absent.

The estimation of naphthalene in coal-gas has been performed by Colman and Smith [1] by passing the gas through a dilute picric acid solution, separating the naphthalene picrate and weighing it, or titrating the excess of picric acid by $N/10$ soda solution. Dickenson-Gair [2] uses a similar method, but employs first dilute acetic acid, before the picric acid, of which a large excess must be taken. An improvement on this method, permitting the estimation by titration, is described by the same author later on.[3]

White and Ball (*J. Gas Lighting*, lxxxviii., 262 and 323) estimate naphthalene by picric acid, like the authors quoted above. To estimate its percentage in tar, they drive it out of this by a current of air at a temperature of 70° to 80° C. and pass the gases through two U-tubes, the first of which, also kept at 70° to 80°, is charged with CaO, glass wool, and P_2O_5, and serves for drying the gases. The second U-tube is placed in ice-cold water and serves for retaining and afterwards weighing the naphthalene (which cannot possibly be a very exact method!).

Uses of Naphthalene.

The naphthalene occurring in such large quantities in coal-tar (usually from 5 to 10 per cent., sometimes perhaps in excess of that [4]) was formerly one of the least welcome of its constituents. It generally accumulated in the creosote oil and caused inconvenience by crystallizing there; sometimes it led to the rejection of creosote oil for pickling timber (pp. 548 and 551). In such cases nothing remained but to work it into the pitch, or burn it for soot, or to employ it as fuel, mixed with coal. Even now crude naphthalene is sometimes employed as fuel in the melted state, for instance for heating the tar-stills. In that case the liquid naphthalene is injected into the fireplace by means of a steam-jet similarly to tar or tar oils (pp. 253 *et seq.*).

[1] *J. Soc. Chem. Ind.*, 1900, 128.

[2] *Ibid.*, 1905, 1279. [3] *Ibid.*, 1907, p. 1263.

[4] Exceptionally coal-tar is found containing hardly any naphthalene. Such has been the case with the Manchester Corporation Gas-works tar in 1873 and 1874, according to Watson Smith. He found naphthalene in cannel-coal tar, along with paraffin. On the other hand, Crace Calvert states the percentage of Newcastle tar = 58 per cent. naphthalene, which is simply absurd.

The applications of naphthalene for the *manufacture of artificial colours* were formerly very few, in spite of the many efforts in this direction; dinitronaphthol (Manchester yellow) and naphthalene red (Magdala red) were for a long time the only colours made from naphthalene. When the series of phthalein colours (eosin, etc.) was discovered, in 1876, a demand for phthalic acid sprang up, for which naphthalene is the starting-point. But far more important in this respect was the discovery of the long series of azo-colours, nearly all of which have come out since 1873. For most of these naphthols, especially $\beta C_{10}H_7(OH)$, are required, and for the preparation of these the purest naphthalene is demanded. Quite recently the manufacture of artificial indigo has been added to the above applications of naphthalene.

One of the most important uses of naphthalene was for some time that for *carburetting gas*. This has been frequently proposed, *e.g.*, by Bowditch (B. P. 2937, 1862); but the principal impetus to this industry was given by the inventions of Livesey and Kidd, afterwards associated with H. Vale, of Hamburg (Ger. Ps. 2075, 8644, 9840, 19012, 32255). Their apparatus, called the "*albo-carbon light*," has been attracting much attention. It is principally adapted for small flames, and is stated to save more than half the gas consumed for the same illuminating power in the best argand burners; so that it is very economical, in spite of the cost of the naphthalene. It is a drawback that, if the apparatus is allowed to get too hot, there is too much volatilization of naphthalene and the flame burns smoky; if it were still further neglected, the naphthalene would boil and the apparatus would burst.

In experiments made by Mr John Pattinson,[1] 1000 cub. ft. of gas, along with 4·63 lbs. of naphthalene, consumed in the albo-carbon lamp, yielded as much light as 2700 cub. ft. of gas burned in fairly good flat-flame burners, or 1780 cub. ft. of gas in argand burners of good construction.

Elster[2] found that 1 cbm. of Berlin gas, carburetted with 53 g. naphthalene, yielded 20-candle power, the hourly consumption per flame being about 100 litres and 5 g. naphthalene. Street-lamps consumed from 110 to 117 litres of gas along with

[1] *Trans. Newcastle Chem. Soc.*, 1882, v., p. 135.
[2] Schultz, *Steinkohlentheer*, 2nd ed., i., p. 199.

5 g. naphthalene, and yielded the light of 16 or 17 candles. On an average the albo-carbon light saved 50 per cent. in gas, and 30 per cent. in total cost. The best effect was produced with small burners. The specific gravity of the gas was raised from 0·38 to 0·60 by the carburetting process.

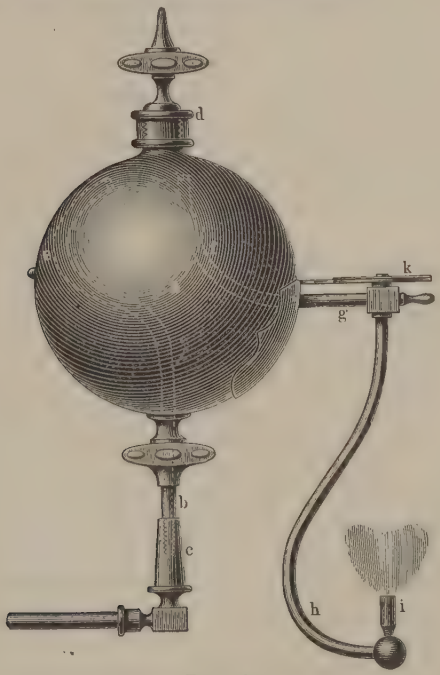


FIG. 166.

Fig. 166 shows the most usual form of albo-carbon lamp. The copper ball *a* is fixed on the socket *c* by means of a stem, *b*, the joint being made merely by true boring-out of *c* and turning *b*; *a* is closed by a screw-cap, *d*, which serves for charging the naphthalene. The gas enters the ball through *c*, *b*, and *e*, and the burner *i* through *f*, *g*, *h*.

Above *i* is fixed the copper disk *k*, which is seen from above in Fig. 167. It will be noticed that by moving the slide *l l*, which revolves about a pivot in the centre, the disk *k*, cut out to correspond with *l l*, is either closed or opened.

The burning gas from *i* heats *k*, which transfers its heat to *a*, and heats the naphthalene contained therein a little above its melting-point, say to 80° or 90°. In consequence of this the gas passing through *a* is charged with naphthalene vapour, which greatly increases its illuminating power. If too much vapour is carried along and the flame begins to smoke, the slide *l l* is moved as in Fig. 167, whereby the heating of *a* is greatly diminished.

In spite of the advantages justly claimed, according to all appearance, for the albo-carbon light, the progress which it has hitherto made, although not inconsiderable (at one of the largest English tar-works the author was informed that in 1886 they made 400 tons of naphthalene sticks per annum for this object), is yet far from being so universal as might be expected; and it has even been abolished again in some cases where it had been introduced. This seems to be mostly owing to the trouble caused by the lighting of the gas. At the commencement, before the naphthalene has become heated, the light is inconveniently small, and some patience is necessary. On the other hand, if the apparatus is allowed to get too hot for one moment, the whole room is for a long time filled with the extremely pungent smell of naphthalene vapour. Of course this can be prevented by careful attention, but such is only too often wanting in the case of the domestics to whom the light must be trusted.

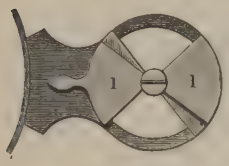


Fig. 167.

The principle of carburetting gas by means of naphthalene is evidently most excellent for enriching very poor gas, such as is obtained by abstracting the benzol from gas by one of the processes mentioned on pp. 38 *et seq.* Davis[1] mentions that such gas, from which 4 galls. of benzol had been extracted per 10,000 cub. ft., and which only possessed 9-candle power, was easily brought up to twenty candles by employing the albo-carbon light; whilst the consumption of gas for lighting a room 10 ft. square was brought down from 23 to about $3\frac{1}{2}$ cub. ft. per hour. This process would also be adapted for making good illuminating-gas from the residual coke-oven gases (p. 119).

[1] *J. Soc. Chem. Ind.*, 1886, p. 5.

A new albo-carbon lamp has been constructed by Kitson & Co. (*Dingl. polyt. J.*, cclxvii., p. 34).

Phillip's Carbo-Oxygen Gas[1] is produced by the combustion of naphthalene, dissolved in petroleum, in a current of oxygen. A lamp suitable for this purpose has been described by Carl[2]; but this process seems to be too troublesome and expensive.

J. W. Sutton (B. P. 4747, 1883) has constructed a somewhat similar apparatus; so also has W. G. Little (B. P. 17108, 1885).

Hempel (B. P. 6463, 1899) carburates spirit of wine by dissolving naphthalene in it. The light given out on burning this mixture is very strong and white.

Chenier and Lion (Ger. P. 144942) employ the vapours of naphthalene and other solid hydrocarbons for heating, lighting, and motor engines.

The Gasmotorenfabrik Deutz applies naphthalene of the ordinary commercial quality for driving Otto gas-motors, with the assistance of a water-bath for fusing it. The consumption is from 260 to 320 g. per h.p. hour, and the blowing-off gases are practically free from soot. Since technical naphthalene is an almost chemically pure substance, there are no rosin-producing constituents which would cause obstructions in the valves and the piston (*Z. angew. Chem.*, 1907, p. 1264).

The Rütgerswerke (B. P. 7594, of 1908) employ for gas-motors a solution of naphthalene in one of the ordinary liquid fuels, prepared by the aid of the waste heat of the motor.

Sudheim and Koppen (Ger. Ps. 6051 and 7784) employ naphthalene in the manufacture of non-phosphorus *matches*.

"*Pantopollite*" is dynamite containing a few per cent. of naphthalene. It was supposed to prevent the formation of nitrous fumes during the explosions; but practical trials have shown that the smell remaining after the explosion was far worse than in the case of ordinary guhr-dynamite.[3]

According to Callenberg (*Prometheus*, 1902, p. 96), naphthalene, if added to the artificial camphor used in the manufacture of celluloids and dynamites, makes these uninflammable and inexplosive.

Traine (Ger. P. 154756) employs a solution of naphthalene in linseed oil in the presence of rosin, as varnish.

[1] *Wagner's Jahresber.*, 1870, p. 728. [2] *Ibid.*, 1872, p. 856.
[3] *Ibid.*, 1876, p. 495.

S. Stein (Ger. P. 23947) makes *porous stoneware* by incorporating with the clay naphthalene suspended in water or suitably dissolved, drying, volatilizing the naphthalene and recovering it at the same time, whereupon the clay is burned in the usual manner. The burned articles show an even porosity; and as the naphthalene does not leave any ash, the pores are not partly filled up with a fusible mass, less capable of resisting changes of temperature.

M. E. Contin[1] makes a specially "*detergent*" *soap* by melting two parts of ordinary soap with three parts of naphthalene. [While it is very doubtful whether such a soap will remove dirt better than the ordinary article, it is certain that those using it will produce an intensely disagreeable atmosphere around themselves!]

Naphthalene is frequently employed for *keeping out vermin* (*e.g.*, moths) and in stuffing animal-skins; Pelouze[2] recommends it for disinfecting purposes generally, Fürbringer[3] especially for water-closets and sick rooms in lieu of carbolic powders. A special investigation of the antiseptic powers of naphthalene has been made by Ernst Fischer.[4] It stops the development of mould and kills the fungi in a very short time, as *Penicillium*, *Mucor*, *Phycomyces*, *Oidium lactis*, the fungus of yeast, the different schizomycetes, etc. Lower animals are driven away or killed; naphthalene therefore serves as a preventive against moths, *Phylloxera*, the insects destroying collections of beetles and butterflies, and any other vermin. Against itch a salve, consisting of equal parts of naphthalene and vaselin, does good service. Naphthalene is excellent for dressing wounds; it suits this purpose quite as well as, or better than, carbolic acid or iodoform, and it is not poisonous like these. It seems therefore called upon to play an important part in medicine and in the household. Furs and woollen clothing, preserved against moths during the summer months by means of naphthalene paper, pertinaciously retain the penetrating smell of naphthalene, and require *long* airing before they are fit to be worn.

[1] *J. Soc. Chem. Ind.*, 1884, p. 353.
[2] *Bull. Soc. Chim.*, 1866, p. 351; 1868, p. 258.
[3] *Berliner klinische Wochenschrift*, 1882, No. 10.
[4] Shultz, *Steinkohlentheer*, 2nd ed., i., p. 199.

Sometimes, according to *Chem. Trade J.*, 1891, p. 304, naphthalene is employed for *pickling timber* by leaving it for an hour or two in a box filled with melted naphthalene. It is said to protect the timber against moisture and insects, but it is not equal to creosotizing for pit-props or for use in water.

Heinrich (Ger. P. 99710) employs naphthalene for a preliminary *tanning* of skins, together with ordinary tanning solutions. It is also used for denaturing dried sheep's intestines, to be imported into Germany.

"*Salubrin*" (*Chem. Zeit.*, 1902, 850) is naphthalene, scented with a little nitrobenzol, to be used as a disinfectant.

Planner (B. P. 26983, 1898) fuses naphthalene or other tar hydrocarbons with camphor (equal parts), adds a disinfecting chemical, *e.g.*, potassium permanganate, and moulds the mixture in a proper way. Or else he cools the naphthalene, reduces it to powder, mixes it with the permanganate, and then fuses the mixture as above.

Kreis (*Chem. Zeit.*, 1905, p. 714) reports that in Basel naphthalene is sold by the name of "Gasin" for increasing the illuminating power of petroleum, and as "Rhodin" for the extermination of vermin.

Genthe (Ger. P. 157542) burns naphthalene to obtain soot, by means of a water-cooled burner.

Traine (Ger. P. 154756) employs naphthalene as an addition to fatty varnishes.

Isleib and Knoche filed an application for the same purpose (Ger. P., appl. I6722), which was withdrawn.

Naphthalene in combination with sulphur is used against the deleterious organisms affecting the vine plant (Haack, *Z. angew. Chem.*, 1909, p. 817).

Statistical.

The quantity of purified naphthalene made in Germany at the present time can be roughly estimated at 10,000 tons. That country in 1904 imported 12,444 tons (mostly in the crude state) and exported 2878 tons of naphthalene; in 1907 it imported 10,144 tons and exported 5980 tons.

Recovery of Basic Compounds from Carbolic Oil.

The oil remaining after extracting the carbolic acid from

redistilled carbolic oil, smelling of bases, and condensing about half the original quantity, was formerly redistilled, and the fraction coming over till 180° was worked for solvent naphtha, of which 90 per cent. distils between 120° and 160°. Since the recovery of benzol from coke-oven gases has been very much extended, large quantities of oils boiling between 160° and 200° are required, free from phenols and naphthalene, and this has caused another process for working-up the above-mentioned oils, in which the bases are also recovered.

The *pyridine bases*, which are now largely used for denaturing alcohol (in Germany and elsewhere), as well as in purifying anthracene, were formerly recovered from the tar formed in the manufacture of bone-charcoal. They can be also obtained from the redistilled carbolic oil, freed from phenols, by agitating with moderately dilute sulphuric acid and saturating the solution with a stream of ammonia, whereupon the bases separate as an oily layer on the top. Or else the acid liquid is neutralized with lime, distilled, and the distillate dehydrated by caustic soda. The same treatment is employed for the oils blown off by steam from the crude sodium phenolate (p. 575), and for the acid-tars from the washing of light oil and first runnings. As these furnish most of the pyridine bases, and as they are much more frequently worked for them than the acid tars from carbolic oil, we shall describe their treatment for that purpose in Chapter X.

After the bases have been extracted from the carbolic oil, it is sometimes treated with quite dilute caustic-soda solution before being redistilled in a light-oil still, with a thermometer. It can serve as an absorbent for coke-oven *benzene* without being washed with concentrated sulphuric acid, as it need not be colourless. The first runnings, say up to 160° or 170°, are combined with a corresponding fraction of the light oil (*cf.* next chapter) and after chemical washing mainly yield ordinary solvent naphtha (120° to 160°), with a little "absorbing" oil. The next fraction is collected up to 215° or 220°, and on distilling in a glass flask shows the desired boiling-points (90 per cent. between 160° and 200°). At first it is but slightly yellow; on being kept for some time it turns darker The residue in the still goes to the creosote oil.

CHAPTER X

LIGHT OIL AND CRUDE NAPHTHA

WE understand by "light oil" that fraction of the first distillation of coal-tar which is midway between the first runnings and the carbolic oil, as mentioned on p. 365. Some distillers term it "first light oils" or "crude naphtha." At some works, especially on the Continent, no such fraction is made, but all the distillates from the beginning up to the "middle oil," *i.e.* up to 170°, are collected in one receiver. The whole of this must then be subjected to the same treatment as will now be described for the "light oil" as defined above.

Light oil in our sense, if collected up to the point at which the distillate sinks in water, has the following properties:—Its average specific gravity is about 0·975; it begins to boil at 95° (the bulb of the thermometer dipping in the liquid); but only a little passes over before 120° is reached, from which point up to 171° about 30 per cent. distils. All that distils above this belongs to carbolic oil. But in order to form a correct judgment as to the quality of light oil, the distillate up to 171° must be rectified. Thus a sample of not very superior light oil yielded in the first distillation:—

Boiling-point.	110°	120°	130°	149°	160°	171°
96°	1	3	4¼	9	16	26½ per cent.

And on rectifying the 26½ per cent.:—

Boiling-point.	98°	100°	110°	120°	130°	188°
90°	1	2	5	9	13	16 per cent.

The light oil of trade is of course the more valuable the larger the proportion of easily volatile matters it contains, supposing it to be unadulterated coal-tar oil. Home-made light oil should give a good yield up to 171°, but little below 120°: the former proves that the receiver had not been changed

too late for carbolic or heavy oil; the latter, that no first runnings have entered into the heavy oil.

Components of Light Oil.

Kraemer and Spilker (in Muspratt-Bunte's *Chemistry*, viii., p. 16) enumerate in what they designate as "light oil" (comprising both our "light oil" and our "First Runnings"):

1st. 5 to 15 per cent. *phenols*, viz., carbolic acid and cresols (principally metacresol), but hardly any xylenols.

2nd. 1 to 3 per cent. *bases*, viz., principally pyridine and its homologues, with a small quantity of aniline, traces of pyrrol, and perhaps of indol.

3rd. 0·1 per cent. *sulphur compounds:* carbon disulphide, thiophen and its homologues.

4th. 0·2 to 0·3 per cent. *nitriles* (acetonitrile and benzonitrile).

5th. 1·0 to 1·5 per cent. *neutral oxygenated compounds:* acetone cumarone.

6th. *hydrocarbons*, forming the principal portion, and composed of:—

(*a*) 3 to 5 per cent. olefins, beginning from hexane.

(*b*) 0·5 to 1·0 per cent. paraffin, from hexane upwards.

(*c*) 1 to 1·5 per cent. non-saturated cyclic compounds, combining at ordinary temperatures with bromine (cyclopentadiene, dicyclopentadiene, dihydrobenzene, tetrahydrobenzene, styrol, indene—the latter sometimes in considerable quantities).

(*d*) Traces of saturated cyclic compounds (hydrindene, etc.).

(*e*) The remainder, *i.e.*, 80 per cent. of the light oil, consists of aromatic hydrocarbons, of which about four-fifths belong to the benzene series and one-fifth to naphthalene and other higher-boiling hydrocarbons. The proportion of the benzene hydrocarbons in what Kraemer and Spilker term "light oil"—that is, in our light oil plus first runnings—is stated by them to be about 100 benzene, 30 toluene, 15 dimethylbenzenes (xylenes), 10 trimethylbenzenes, 1 tetramethylbenzenes, traces of higher methylated and ethylated benzenes.

The *testing* of light oil is usually confined to its specific gravity, by means of the hydrometer or Mohr's balance, and its boiling-points, *i.e.*, the fractions which it yields at stated

intervals of temperature. This is carried out in the same manner and by the same apparatus as will be described later on in this chapter and the next chapter for testing crude benzol. Sometimes the light oil is also tested for its percentage of phenols (by shaking with caustic-soda solution, *cf.* p. 607), and of bases (pyridines). This is done after extracting the phenols by shaking 100 c.c. with 30 c.c. sulphuric acid of sp. gr. 1·15, evaporating the acid solution on the water-bath until the addition of water does not produce any cloudiness, adding concentrated caustic-soda solution and measuring the volume of the bases now separating. If the pyridines suitable for denaturing purposes are to be estimated separately, the cadmium chloride test described at the end of this chapter is applied.

Applications of Light Oil as such.

A good deal of light oil is without purification—*e.g.* for illumination in excavations (where the smoke is of no consequence), for thinning down heavy oil or liquefying pitch to make "refined tar," and especially for preparing varnishes for wood and iron (pp. 441 *et seq.*). Thenius[1] makes from it "varnish oil" by treating it several times with potassium bichromate, manganese, and sulphuric acid, then with water, at last with caustic-soda liquor, and subsequently distilling. Thus a limpid oil of sp. gr. 0·880 is obtained, which does not turn yellow in the air and is an excellent solvent for rosins like sandarac, mastic, or copal; so that superior varnishes for photographers and printers, cart-grease, lubricating oil, etc., can be prepared with it, for which special prescriptions are given.

Rectification.

Most of the light oil is rectified, at first by direct fire; only at smaller works is steam used for this product. Along with this oil is worked up the oil obtained on treating the carbolic oil with caustic-soda solution, after removing the latter (pp. 575 and 669).

The object of this first rectification cannot be exactly the

[1] *Verwerthung des Steinkohlentheers*, p. 62.

preparation of commercial products; for this the composition of light oil is still too complicated. For similar reasons it was formerly believed that it did not pay to wash it chemically, except when it had been purposely collected up to the point at which it contains much carbolic acid; and frequently even then its last portions only were treated with alkali. Hence the usual object of rectifying it is, on the one hand, to obtain the most volatile oils (which belong to the same class as the "first runnings" and are treated along with these), and, on the other hand, to separate the heaviest oils which promise no further yield of benzol and go better to creosote or carbolic oil. Between these two a fraction necessarily remains which exhibits some of the characteristics of either. This is always put back into the still and distilled with light oil; so that the latter is finally completely split up into the two products mentioned above, although in each single operation three products are obtained, which we call light-oil naphtha, secondary light oil, and residue. This leads almost universally to making two fractions in the distillation of light oil, and running the third product, as residue, directly out of the still. The question can only be, where to set the limits. Evidently, if the residue is to go to creosote oil, the distillation must be continued till no appreciable quantity of light oil remains behind; and this indicates the limit between the second and third fractions. Where the residue goes to carbolic acid, not even the above is of consequence, since the alkaline treatment in any case separates the hydrocarbons contained in it. In the former case the usual test is, to work till the distillate begins to sink in water; in the latter case the thermometer is usually consulted (see below).

It may be more uncertain where to set the limit between the first and second fractions. Evidently this does not matter very much, since the second fraction is always redistilled. Some English tar-distillers go by the hydrometer, and change the receiver when the distillate shows 10 degrees "under-proof" (*i.e.*, sp. gr. 0·932), at which point about one-fourth part of the light oil has distilled. The second fraction is collected till it begins to sink in water, which corresponds to another 25 per cent., sometimes to 50 per cent. of the light oil.

The first fraction ("light-oil naphtha" or twice-run naphtha")

from light oil obtained in the first distillation of tar shows, for example :—

	Boiling-point.	Per cent. distilling at								
		28°	100°	110°	120°	180°	188°	149°	160°	171°
1	92°	...		2½	9	20	33	50	64	78
1*a*	84°	2½	5	12	24½	33	39	...	...	...
2	107°	...	...	1	5	17	29	47	64	79
3	104°	...	...	½	3	10	21	44	63½	78
3*a*	98°	...	4	...	...	...	...	...	...	...
4	101°	...	...	4	19	38	52	68	79	90
5	107°	...	...	1	5	17	29	47	64	79

1*a* is the result of rectifying the first 50 per cent. of 1 ; 3*a* that of rectifying the first 50 per cent. of 3. According to this there are great divergencies in the intermediate product; but finally in all cases, nearly 89 per cent. has come over at 171°. The distillations 1*a* and 3*a* show that from light oil toluene, xylene, etc., can be obtained, but no considerable quantity of benzene.

The oils taken off from sodium phenate naturally show rather higher boiling-points, as proved by the following example, where 1 indicates the distillation of the oil itself, 2 the rectification of the first 41 per cent. :—

	Boiling-point.	Per cent. distilling at								
		98°	100°	110°	120°	180°	188°	149°	160°	171°
1	118°	...	...	...	...	6½	21	41	58	72
2	...	...	...	5	15	25	32½	...	...	...

Davis[1] quotes the following tests of "twice-run naphtha" :—

	Spec. grav.	Per cent. distilling at					
		100°	110°	120°	140°	170°	200°
a	0·878	0	17	41	72	94	99
b	0·888	3	23	46	71	88	95
c	0·901	2	20	40	62	80	90
d	0·904	0	9	29	57	81	95

[1] *J. Soc. Chem. Ind.*, 1885, p. 646.

Muspratt-Kerl's *Chemie* (vi., p. 1175) quotes the following statements from South-German (1) and North-German (2, 3) works :—

	Per cent. distilling at				
	100°	180°	140°	180°	200°
1	10·6	25·0	...	38·9	57·2
2	15·4	...	22·5	44·0	...
3	20·3	...	27·12	50·0	...

No doubt the "light oil" in this case comprised both first runnings and our light oil together.

Already from these laboratory tests it is evident that the distillation of light oil is best guided by the thermometer. The first fraction might be made up to 170° and worked along with the first runnings from the tar; the second fraction is made at 205° or 210°, the product reworked, and the residue run to carbolic oil. According to Wurtz,[1] the fraction of coal-tar distilling between 150° and 200° (roughly corresponding to our light oil) is worked up thus :—

First Rectification.

a. Fraction up to 120° goes to the corresponding fraction of the principal distillate, received up to 150°.

b. Fraction between 120° and 190° is washed with acid and alkali, then rectified.

c. Residue (above 190°) goes to creosote oil.

Second Rectification (of the fraction *b*).

a. Product up to 120° contains benzene and toluene, goes to the corresponding products from the first runnings.

b. Product from 120° to 127° yields solvent naphtha No. I.

c. „ „ 127° to 140° „ „ „ „ II.

d. „ „ 140° to 150° „ „ „ „ III.

e. Residue goes to creosote oil.

The product distilling from light oil at 170° to 210°, and above called "secondary light oil," is sometimes employed for washing anthracene (p. 486); or it is chemically washed and rectified, so

[1] *Dictionnaire de Chimie*, i., p. 1633.

as to yield solvent naphtha, and absorbing-oil for coke-oven benzene.

W. Feld (Ger. P. 208190) purifies tar oils, intended for the recovery of sulphur from SO_2 and H_2S according to his Ger. P. 202349 (in which case the sulphur sometimes turns out discoloured), by a previous treatment with H_2S and SO_2, and subsequent distillation.

Stills for Light Oil.

The rectification of light oil is effected in wrought-iron stills, usually constructed and set exactly like tar-stills. The bottoms are, however, never made so much curved-in as shown in Fig. 84, p. 327, because much less is left in the still when distilling light oil than when distilling tar. Only at the largest works are they made as large as the tar-stills; at others a small size suffices, as only a small percentage of the tar passes through them. *E.g.*, a still 5 feet wide and 6 feet high suffices for four tar-stills of twice the height and width. It is preferable not to go below the size just mentioned, even at smaller works, but rather to work the still less frequently, or employ it at the same time for the first rectification of the crude benzol. The reason for this is that such a still, holding about 750 gallons, can be easily worked off in a working-day, say seven to nine hours, and allowed to stand overnight, to cool down the residue before running it out. The still-top is covered with brickwork or some non-conducting material. The still-head is made of cast-iron, and is connected with a 2-inch lead worm, ending in a $1\frac{1}{2}$-inch lead worm, the lower part of which may be only 1 inch wide. A condensing-tub 4 feet wide and 6 feet high suffices for such a still. It should be separated by a wall from the still, likewise the two receivers for naphtha and secondary light oil; the discharge-cock also is best made to pass through the wall, so that all these parts are away from the fire and can be seen at a glance. Fig. 168 shows this arrangement.

The discharge-pipe for the residue can be provided with a screw-thread, in order to connect it directly by means of a pipe with the tank for carbolic or creosote oil. This is suitable, because the residue is very hot, even after standing overnight, and gives out very acrid and disagreeable vapours.

Of course the usual mountings must be provided, such as manhole, feed-pipe, air-vent, and thermometer; a simple safety-valve (p. 337) is also advisable.

When *working a light-oil still*, a brisk fire is made at first; but this is moderated as soon as the distillation begins, and can be raised again later on. Here, too, some water comes at first; but ceases again after a short time. As long as naphtha comes over, say up to 150° or 170°, cold water must be run through the condensing-tub; but after this the water in the latter and the distillate should be allowed to get warm, because very much

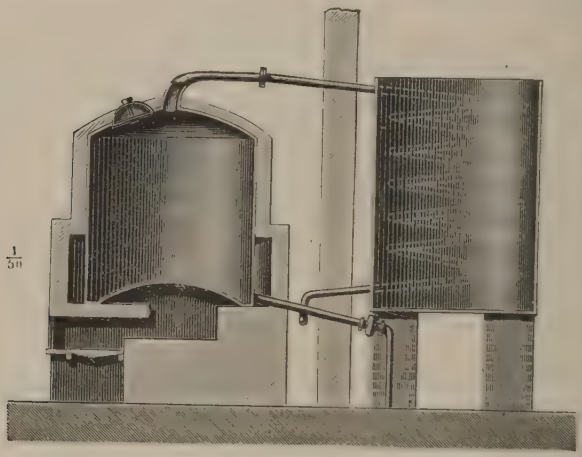


FIG. 168.

naphthalene comes along, and might choke up the worm if it solidified. We have seen (p. 645) that it is still more necessary to prevent this when distilling the oil taken away from sodium phenate. Special care should be taken to arrange the end of the worm so that the distillate can run out completely; otherwise, at the end of the operation a plug of naphthalene will be formed there, which might be overlooked in starting a new operation, and might lead to awkward consequences, especially in the absence of a safety-valve. It even happens, if the still is cooled down too much before discharging, that the residue solidifies entirely and cannot be run out without warming the still again.

Some manufacturers prefer heating the light-oil still by indirect steam; but this does not seem to offer any advantage. It is useful, however, already at this stage to substitute for an ordinary still-head a dephlegmating column, so as to effect a better separation of the product, as we shall see in the next chapter. This is especially advisable when first runnings and light oil are rectified together.

Manufacture of Benzoic Acid from Light Oil.

Benzoic Acid, which had been found in the residues from the carbolic acid manufacture by K. E. Schulze, and which is formed from the benzonitrile present in the tar oils, can be manufactured from light oil according to the Aktien-G. f. Teer- u. Erdöl-Industrie (Ger. P. 109122) by the following process. The fraction boiling between 150° and 240° C. is freed from phenols by washing with caustic-soda solution, sp. gr. 1·10. The oil is now heated by injection of steam with about twice as much caustic-soda solution, sp. gr. 1·4, as is required for saponifying the benzonitrile present, in a still provided with a steam jacket and inside open steam-pipe and a stirring apparatus, until all the ammonia is expelled. This takes a few hours. The distillate contains the more volatile oils and ammoniacal liquor. The liquid remaining in the still on cooling separates into an oily and an acqueous portion. The latter is treated with gaseous CO_2, until the excess of NaOH has been saturated, and the small quantity of phenols, appearing as an oily layer on the top, is removed. The clear aqueous liquid is an almost chemically pure solution of sodium benzoate, from which benzoic acid is obtained by adding a stronger acid in the shape of fine white crystals.

First Runnings (Light Naphtha).

This term is applied to the first and lightest distillate from the tar-still which come over together with some (ammoniacal) water, as described on p. 363; and we shall now show how it is further treated. This fraction is sometimes called first light oils, or once-run naphtha, or crude naphtha, etc. Where no such fraction is made, but the light oil is collected all together, it is generally redistilled over a direct fire; and the "twice-run

naphtha" or "light-oil naphtha" thus obtained is treated in a similar way to that now described for our "first runnings."

The latter product contains of course the most volatile constituents of coal-tar, as enumerated in the second chapter; but along with them, owing to the peculiar nature of fractional distillation, there are considerable quantities of less volatile bodies. Hence we find in it not merely benzene and its homologues, but sensible quantities of thiophens, of phenols, naphthalene, aniline and other bases, empyreumatic resins, etc. Some of the most volatile bodies are impurities to be removed as completely as possible, as methane homologues, thiophens, olefins, carbon bisulphide, mercaptans, nitriles. The "eupion" sometimes mentioned, and Mansfield's alliol, will have to be sought among the latter class of bodies.

Since a distinction or separation of all these bodies is not to be thought of, least of all for technical purposes, it is usual to estimate the quality of first runnings by fractional distillation exactly in the same way as described above (p. 666) for light oil, rectifying again the more volatile portion. The following table shows some of the results thus obtained, in percentages by volume:—

No.	Boiling-point.	88	93	100°	110	120	130	138	149	160	171	Sp. gr.
1	79°	1	2½	4½	12½	22½	31	37	45	52	62	0·906
2	84°	1	...	15	30	43	51	57	63	69	77	...
3	98°	...	...	2	...	27	43	54	63	73	83	0·905
3*a*	...	...	3	15	...	...	...	...	...	...	...	...
4	91°	...	3	10	26	38	49	55	63	71	78	0·908
5	89°	...	½	5	34	45	55	61	68	73	78½	0·911
5*a*	...	...	9	27½	40	47½	...	...	...	...	...	...

In all these tests the thermometer-bulb at the beginning of the distillation was just immersed in the liquid; the "boiling-point" is consequently much higher than the temperature at which the vapours actually passed over; and even the later temperatures are no doubt too high. 3*a* is the result of rectifying the first 45 per cent. of 3; 5*a*, that of the first 61 per cent. of 5.

The table shows that the composition of first runnings varies very much, especially at the lower temperatures, without being

indicated by the specific gravity. In fact, the latter is quite worthless for the estimation of the commercial value of crude naphtha. A single distillation of the latter does not suffice; and in any case that which has passed over up to 130° should be rectified. Even then the results differ considerably if, as is usual in England, the thermometer-bulb is immersed in the liquid, according to the size of the retort, the quantity of the liquid, etc. The only reliable plan is to place the mercury-

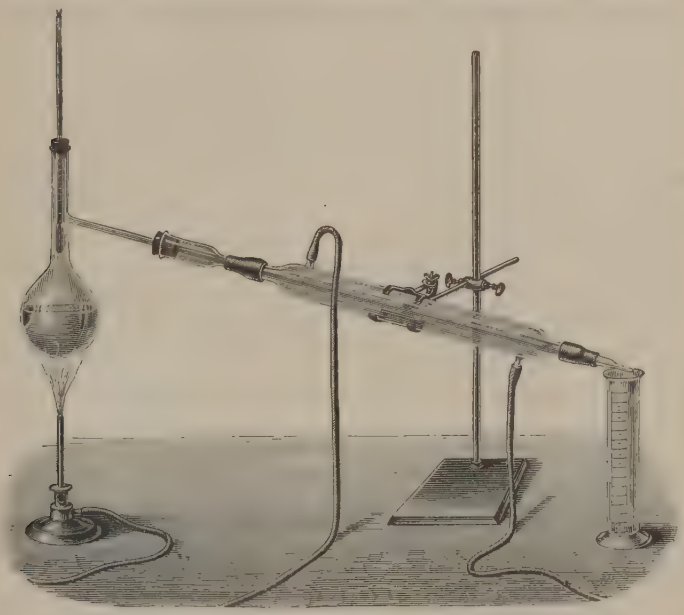


FIG. 169.

bulb at the height of the vapour-delivery tube; and it is even preferable to work with a proper fractionating-flask connected with a Liebig's cooler (Fig. 169); best of all with a dephlegmating head, such as Linnemann's three-bulb apparatus (*cf.* next chapter). It has been found the most suitable plan to place the mercury vessel exactly as figured here—that is, its top on a level with the bottom of the side-tube.

More accurate methods for testing the value of crude naphtha will be described at the end of Chapter XI.

Good first runnings in the first distillation ought to yield at least 10 per cent. by volume up to 100°; in rectifying the product distilled up to 130°, at least 25 per cent. should come over up to 100°. Up to 171°, on an average 78 per cent. comes over.

Watson Smith found the following results of first runnings from Wigan cannel-coal tar (p. 412):—

Below	130°	130-140°	140-150°	150-160°	160-170°	170-180°	180-190°
Per cent.	15	20	10	6	9	7	11

Hohenhausen[1] quotes the following tests:—

A. *English Naphtha.*

Centigrade.	Wigan. Per cent.	Yorkshire. Per cent.	Scotland. Per cent.
105°	...	4	...
110°	4	16	17
120°	19	34	38
130°	33	47	49
140°	45	...	58
150°	55	...	69

B. *French Naphtha.*

Centigrade.	D'Anzin. Per cent.	Blanzy. Per cent.	Comp. Par. de Gaz. Per cent.
100°	5	14	10
120°	24	37	23
130°	39	49	55
140°	50	59	75
150°	60	69	90
160°	67	77	98
170°	75	85	...

Davis (see below) quotes as the average of many examples of first runnings from different parts of England:—

Sp. gr.	100°	110°	120°	140°	170°.	200°
0·905	2	14	33	57	80	92

Washing with Chemicals.

The first runnings, as well as the light-oil naphtha, which is chemically quite analogous to it (*cf.* pp. 668 *et seq.*), is nearly always "chemically washed" before any rectification, *i.e.*, treated with

[1] *J. Soc. Chem. Ind.*, 1884, p. 73.

strong sulphuric acid and alkali, less frequently with oxidizing agents. Formerly the greatest stress was laid on washing the naphtha with *strong sulphuric acid*, and this treatment was applied to the naphtha first and foremost. It was always followed, first by washing with water and then with a solution of alkali, before proceeding to the final treatment in the steam stills. In that style of proceeding the phenols could not be recovered, since they are (together with the naphthalene) converted into sulphonic acids which remain dissolved in the dirty acid (acid-tar). The pyridine bases were, of course, also taken up by the sulphuric acid, but it would be difficult to recover them from the dirty acid, and this was never even attempted on the large scale at that time, as there was no use for those bases. The sulphuric acid also takes up the olefins and part of the thiophen and its homologues, a little acetone, other ketones, nitriles, etc.; it destroyed empyreumatic resinous substances, and so forth. It acts also upon the valuable substances, viz. benzene and its homologues, but at the ordinary temperature only to an insignificant extent; if no more acid is employed than is necessary, still, as this action is never entirely absent, it should not be prolonged beyond necessity, and no excess over and above the quantity required for purification should be employed. Used in excess, sulphuric acid forms "sulpho-oils," *i.e.*, partly sulphonic acids, partly sulphones, *e.g.*, $(C_6H_5)_2\ SO_2$, which to some extent remain dissolved in the hydrocarbons and are afterwards very troublesome, especially in burning. I have experimentally proved[1] that, under the same circumstances, the action of sulphuric acid in dissolving the benzenoid hydrocarbons is stronger in the case of the higher homologues than with benzene itself. When treated for five minutes with 5 per cent. of strong sulphuric acid, benzene loses 0·1 per cent. (when quite free from thiophen, even less), but xylene 0·25 per cent. The quantity of hydrocarbons dissolved increases with the quantity of acid employed and with the temperature. After being treated with sulphuric acid, benzene assumes a yellowish, toluene a greenish, xylene a pink colour; but all of these vanish after washing with water. Kraemer and Spilker have shown that one of the principal actions of sulphuric acid is the condensation of cumaron, indene, and cyclopentadiene into resinous

[1] *Chem. Zeit.*, 1883, pp. 5 and 57.

polymers, and a molecular combination of styrolene with the methylated benzenes (*cf.* p. 222). The reaction is not yet cleared up in all particulars, but evidently differs with the difference of the substances. Cyclopentadiene (b.-p. 40°) and dicyclopentadiene (b.-p. 170°) are transformed into a dark brown resin, insoluble in all solvents, which soon separates from the sulphuric acid and transforms this into a magma, so that great haste is necessary to draw off the acid. The olefines at first simply add H_2SO_4, forming ether-sulphuric acid, which partly remains dissolved in the sulphuric acid, partly reacts with another molecule of the olefine, forming a neutral sulphuric-acid ether or else splitting off sulphuric acid and forming a polymeric olefine. Other substances may be again formed from these, but probably the polymeric olefines are formed in the greatest quantity. They remain dissolved in the benzol and are found in the residue when fractionating it. The free ether-sulphuric acid is decomposed, when afterwards water is applied for washing with formation of an alcohol:

$$C_6H_{12}\begin{matrix}-OH\\-SO_3H\end{matrix} + H_2O = C_6H_{13}(OH) + H_2SO_4.$$

The application of *alkali* (practically always caustic soda) is quite as indispensable in the case of first runnings as in the purification of petroleum, paraffin oil, or the heavier coal-tar oils, although the first runnings contain a much smaller quantity of phenols, the removal of which is the principal object of this treatment. This made it possible, and formerly most usual, to commence the washing with sulphuric acid and end with weak caustic-soda liquor. The latter can in no case be dispensed with entirely, as it must remove the remaining phenol and every remnant of sulphuric acid and sulphonic acids.

Recently it has become most usual to *commence with the alkaline treatment.* This allows of recovering the phenols, and is evidently quite indispensable when first runnings and light oil have not been separated in distilling but are washed together before rectifying. It must, moreover, be borne in mind that the phenol contained in first runnings is mostly real carbolic acid, and is all the more valuable because of this. On the other hand, it has been asserted that phenol made from first runnings alone has a very disagreeable smell, and very probably this is

really the case; but this objection is avoided if the alkali previously used for washing first runnings is mixed with fresh caustic-soda solution, and is subsequently employed for washing light oil or carbolic oil, as described on pp. 567 *et seq.* On the whole, it seems advisable to proceed in this way; that is, to begin with alkali of, say, sp. gr. 1·15; then comes sulphuric acid of about 1·3 sp. gr., to extract the pyridines; this is followed by a treatment with strong sulphuric acid, sp. gr. 1·84, to remove the non-saturated hydrocarbons, etc.; and the last washing takes place with a weak solution of caustic soda.

The mixing-apparatus for the chemical treatment of crude naphtha must, of course, be proof against the action of acids and alkalies. Usually it is made of wood or sheet-iron lined with lead, the sheets of lead being burned together by the hydrogen-blowpipe. The lead may be $\frac{1}{4}$ to $\frac{3}{8}$ inch thick. But at some places cast-iron vessels are preferred, which do not so frequently need repair as leaden ones. Cast-iron is but little acted upon by the strong vitriol, and is even less so when the latter is charged with tarry matters. Hence cast-iron machinery can be employed for agitation (mixing); and the discharge-cocks may even be made of brass or gun-metal, which would be impossible in the case of pure acid.

The mixers must be well covered over, to prevent the benzol from volatilizing during the operation. In the case of hand work this cannot be carried out so completely as with mechanical stirring, where the shaft passes through a stuffing-box and special pipes are provided for running-in the naphtha, acid, water, and alkali.

The discharge-cocks should always be so arranged that the dirty acid, as well as the water, can be run out to the last drop. For this purpose the bottom is made to slope to one side, and the cock is fixed in the lowest part in such a way that no portion of it projects upwards; so that any mixture of the liquids in running out can be entirely avoided with some little care.

At small works the mixing of the naphtha with the chemicals or the water can be done sufficiently by hand, especially as only a small percentage of the tar is subjected to it. This is performed by means of wooden rakes, the head of which is about 15 × 6 ins., and is perforated with six or eight 1-in. holes; with these the

attendant constantly fetches the acid, etc., up from the bottom, which mixes it much better than mere stirring. This should be continued for an hour, or for half an hour at least. In this case the mixer may be circular or square, whilst for mechanical mixing it should be circular. It should be only three-quarters filled with the naphtha to be washed.

Evidently mixing by hand is very inferior to *mechanical mixing*, which is, indeed, preferred at all larger works. Sometimes it is done by a finely divided current of air (as described, p. 573, for carbolic oil); but most manufacturers prefer agitating by machinery, because the current of air carries away some benzene. This cannot amount to very much, as the mixing need not last above ten or fifteen minutes. We shall mention only some of the most usual mixing-machines. We have already (p. 572) spoken of Hübner's machine, constructed like a churn, in which the mixing is effected by a perforated piston, moving up and down, similar in principle to the mixing by hand with perforated rakes just described. A similar principle was employed in Jung and Must's apparatus,[1] with the exception that the motion was not communicated by gearing, but by a steam-cylinder placed directly on the mixer, the piston being attached to the same rod as the mixing-disk. Rolle's mixing-machine[2] consists of a sloping cast-iron cylinder, whose centre of gravity is situated in the agitating-shaft, provided with scoops for catching the acid and alkali, which, owing to their higher specific gravity, move at the periphery. This machine, as well as that constructed by Vogt,[3] seems less adapted for our purpose than either Hübner's or Jacobi's.[4] In the latter (Fig. 170) the cast-iron cylinder, *a a*, is surrounded by a wrought-iron steam-jacket, *b b* (which can be dispensed with for naphtha, but is indispensable for carbolic acid, naphthalene, etc.), and has a conically shaped bottom. In this tapering part revolve the blades of a horizontal shaft, *c*, which is moved by a lateral vertical shaft, *d*, so that the contents of the mixer are quite accessible. In the arrangement shown in the diagram no

[1] Described by Fuhst, *Dingl. polyt. J.*, clxvi., p. 21.

[2] *Wagner's J.*, 1862, p. 680.

[3] *Dingl. polyt. J.*, clxvii., p. 261; Jacobi (*ibid.*, clxviii., p. 264) declares it to be quite useless.

[4] *Dingl. polyt. J.*, clxviii., p. 261.

stuffing-boxes are employed, because the packing could not be made to stand the action of acids, and the latter soon corroded the journals so that no tight joint could be effected. Lining with lead or asbestos packing did not prevent this in the case described by Jacobi, but I have seen several cases where it has been successful. The steam for heating enters at *f*, and the condensation-water issues at *g*; *h* shows the level of the liquid; *i* and *k* serve for discharging the oil and the washing-agents. The vessel *a a* should be cast in one piece, and with the bottom turned downwards, in order to avoid flaws, which would be very

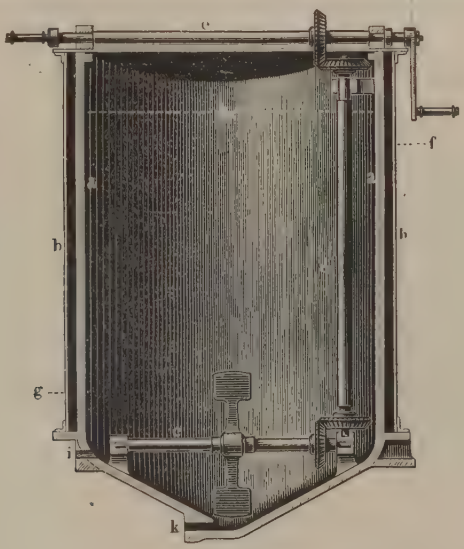


FIG. 170.

injurious in presence of the acid. The shaft *e* revolves forty-five or fifty times, the agitating-shaft *c* sixty-four or seventy-two times per minute. This apparatus, which holds 3 tons, can be set in motion by two men, without any steam-power, as the mixing only lasts a few minutes at a time.

A very efficient form of mixer is shown in Fig. 171. The mixing-vessel contains a smaller cylinder, open at top and bottom, and in the centre there is a spindle, carrying an Archimedian screw. By the revolution of the latter the acid or

alkaline liquor, which is always at the bottom, is raised up in the inner cylinder and poured out over the top into the naphtha contained in the outer vessel. As it sinks down, it is caught up again by the screw, and thus a very good mixture is effected.

A similar mixer of special construction has been patented by Burt, Boulton, & Haywood, and E. R. Garrett, and is shown in Figs. 172 and 173, where the liquid can be made to move either in an upward or a downward direction.

The mixer should be placed at a sufficient elevation to run both the acids and other liquids into suitable places. The dirty acid is sometimes emptied into carboys, but is usually carried away to an outside tank by a lead spout.

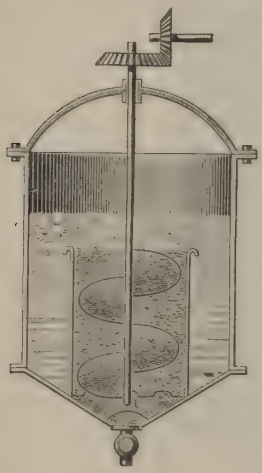


FIG. 171.

The washing-water is not run straight away, as it is next to impossible always to prevent a little oil from coming along with it. This oil can be saved by the drain commencing in the mixing-house itself with a catch-pool, in which the washings are first collected. The floor is made to slope from all sides towards this catch-pool, so that any oil spilt anywhere can be washed into it. The liquid does not run into the drain from the top of the catch-pool, but through a pipe reaching nearly to its bottom, bent at an angle at the top and passing through its side into the drain. Since the drainage thus takes place from the bottom of the catch-pool, the oil remains quietly at the top, and is taken off from time to time.

The *operation of mixing is performed in this manner* :—When the naphtha has been pumped into the mixer, it is first allowed to rest quietly for some time; and the never-failing water, which collects below, is completely drawn off before adding the washing chemicals, which would otherwise be diluted. A careful workman can, in this and all similar cases, run off the water without a drop of oil, by cautiously regulating the tap, observing the colour, and touching the liquid with his finger.

If any oil should run off through some mishap, it is retained in the catch-pool.

When it was usual to commence the chemical washing with strong oil of vitriol, the previous removal of the last traces of water from the naphtha was very important indeed. When, however, beginning is made with an alkaline treatment (*supra*, p. 678), it is not quite so important to remove the last traces of water before this, but all the more so before proceeding to the treatment with concentrated sulphuric acid.

The *quantities* of alkali and acid used for chemical washing should be fixed by preliminary tests performed in the laboratory,

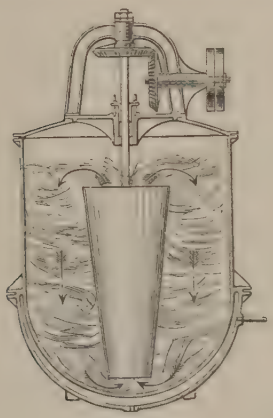


FIG. 172.

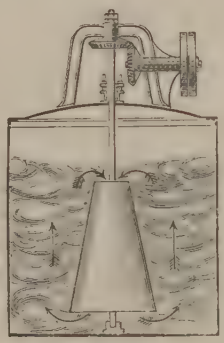


FIG. 173.

as described on p. 568. Of course there must be always more taken than is just necessary for effecting the chemical reactions, more especially as these are partly of a complicated and varying character, more especially in the case of concentrated sulphuric acid (*supra*, p. 677).

After completing the alkali treatment, we come to the treatment with *sulphuric acid*. When, as now usual, the *pyridine bases are to be recovered*, the first acid employed is only of sp. gr. 1·3, as we shall see in the last part of this chapter. After this follows a treatment with 1 per cent. acid of sp. gr. 1·7, which is meant to take up the water, and this is again followed by the proper treatment with acid of sp. gr. 1·84, of which

enough must be used to effect a thorough purification. We may commence with 2 per cent. of this strong acid, agitate for ten minutes, allow to settle, draw off the acid-tar (which occupies about twice the volume of the acid employed), add another 2 per cent. strong acid, and proceed as before. After this we should test the naphtha in the laboratory (which can be done during the hours required for settling) in the manner to be described hereafter, and if this test shows the necessity of applying another per cent. or two of strong acid, this must, of course, be done, before running the purified naphtha into another washer, where it is treated, first with water and then with dilute caustic liquor, as described below.

With a mixing-machine, 10 or 15 minutes suffice for thoroughly churning up the chemicals with the oil. After this at least 3 hours must elapse to allow the liquid to settle. It is best to mix at the end of the shift, and to let the liquid settle overnight, but not any longer, because otherwise the dirty acid turns so thick that it will not easily run out; sometimes great lumps of a pitch-like substance are formed, which choke up the tap. If the acid is too thick even after shorter settling, this is a proof that very many impurities were present—*e.g.*, tar which frothed over into the first runnings, or light oil from the light-oil still. In such a case more acid should have been used, and more alkali will have to be used afterwards. Thus even previous mistakes of the men can be subsequently discovered. On the other hand, if the dirty acid is too thin, this is a sign that too much acid has been used, or that the water had not been completely run off previously. Neither of these ought to occur. Generally the acid will be found to have doubled its bulk by taking up tarry matters.

Kusch (Ger. P. 181255) describes a process for facilitating the separation of the resinous masses separated from the tar oils by the action of strong sulphuric acid. His apparatus allows of heating the lower portion of the resinous mass and thus making it more fluid, while the upper portion is kept cool and more viscid, so that the mass is prevented from rising upwards into the oil. The greater fluidity also facilitates the drawing off of the acid-tar.

The acid should be run out to the last drop: the bottom of the mixer must be constructed accordingly (p. 681); for any

remaining acid, on being diluted with the washing-water, separates a large portion of the dissolved bodies and thus contaminates the naphtha over again, certainly more mechanically than by solution, as the tarry matters, when changed by sulphuric acid, are hardly soluble in naphtha. For this reason alone the *dirty acid* or *waste acid* (sometimes called *acid-tar*) must never be run off through the catch-pool and common drain (p. 682), which would be stopped up directly; it must be run by an open shoot into a special tank, or into carboys, tanks, etc. Wooden casks last some time, as the corrosive action of the acid is greatly weakened by its tarry admixtures; but they are acted upon in time. The acid should never be run straight into a public watercourse, as it is fatal to all animal life.

V. Falke[1] proceeds as follows in order to prevent naphtha from being carried away by the last portions of the acid in the form of an emulsion, and at the same time to avoid the contamination caused by adding water to the naphtha still containing acid. After having drawn off the first vitriol-tar, he agitates the naphtha for 15 minutes with 0·5 per cent. sulphuric acid at 142° Tw., draws off this acid, and repeats the operation with acid of 106° Tw. By diluting the strength of the waste acid in this manner, it is possible to remove the last traces with water or alkalis, without forming an emulsion.

When the acid has been drawn off, *washing with water* follows. Water amounting to about one-fifth of the bulk of the naphtha is run in, mixed up with it for a quarter of an hour, and allowed to settle for half an hour. The water, which has now acquired a deep red colour, is run off by the bottom tap, every precaution being taken against oil coming along with it, and flows away through the catch-pool sunk in the floor of the house (p. 682). This operation is repeated three or four times, and, if the fourth water is still coloured, even a fifth time. Even the fifth water tastes rather bitter, perhaps from naphtha; it may also react very faintly upon litmus; but it ought in no case to show any colour.

These washing-waters are utilized for diluting the strong acid-tar, which thereby separates in two layers. The bottom layer consists of a tolerably pure, although brownish acid of sp. gr. 1·30 to 1·35, which is used for extracting the pyridine

[1] *Chem. Zeit.*, 1885, p. 1869.

bases, or in the ammonium-sulphate department of the factory. The upper portion is a thick solution of resin in benzol, containing some substances in suspense. It must anyhow not be run away, on account of its noxious properties, but neutralized with lime, whereupon the benzol may be recovered by a treatment with steam. The residue remaining behind is a resin, almost solid at ordinary temperatures, which may be used as a kind of asphalt for pavements, etc.

New Processes for washing Crude Benzol.—Fritz Schwarz (Ger. P., March 12, 1904) applies sulphates in addition to sulphuric acid; preferably a mixture of fuming sulphuric acid with sodium or potassium bisulphate.

Glaser and Bürstenbinder (Ger. P., appl. C15062, class 12) apply, after the usual washing with sulphuric acid, another washing with hydrochloric acid, whereby the hydrocarbons are obtained almost entirely devoid of smell.

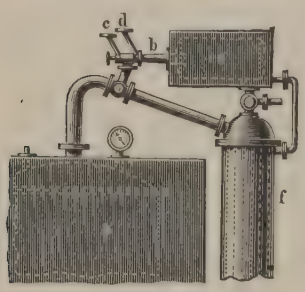


FIG. 174.

The *last operation* is the second alkaline treatment with dilute caustic-soda solution, say, sp. gr. 1·100. This liquor is gradually added during the agitation until a change of colour takes place in the tar oil, when nothing further is added. Usually the colour changes from reddish brown to light brown or brownish yellow, and that very abruptly; but sometimes blue or purple colours are observed. Finally the liquids are well mixed up, and then left for an hour to settle; the caustic liquor is drawn off from the bottom; the naphtha is twice washed with water, and is now ready for distillation. In Lancashire sometimes milk-of-lime is used instead of caustic soda.

H. Hirzel (Ger. P. 34315) combines the distillation of the oils with the chemical washing in one operation, by intimately mixing the vapours of light oil, etc., with the chemicals (acid, caustic liquor) in the state of a spray. In Fig. 174, *a* is the still, *b* the injector (spray-producer), *c* the pipe conveying the steam, *d* that conveying the chemical agents, *e* the preliminary water,

f the proper condenser. This process has not met with any extensive application.

The *loss in chemical washing* amounts on an average to 8 per cent. by volume of a mixture of first runnings and light-oil naphtha. Good oils lose only 5, or even 4 per cent., bad ones as much as 12 per cent. Fresh products require less chemicals than old ones, and lose less by the treatment. Careless working, where much naphtha runs away with the water, may double or even more than double the loss; and even the catch-pool does not quite prevent this, as some of the naphtha remains suspended in the water.

The yellowish *colour* of the crude benzol is changed by the action of sulphuric acid on certain of its impurities into a purple, or else into a brown-red shade, but this goes away during the subsequent operation, and gives place to a slightly milky appearance and yellowish-brown colour.

When testing purified naphtha by distillation, the boiling-points are usually found rather higher than those of the unwashed naphtha. This proves that the removal of less volatile bodies (phenols, naphthalene, bases) is more than compensated by that of more volatile ones (methanes, olefins, sulphur compounds). Complete purification, so that nothing but benzene and its homologues remain, cannot be expected; carbon bisulphide especially remains, often in very appreciable quantities; and even the "chemically pure" descriptions of benzene, toluene, etc., formerly, till Victor Meyer's discovery of thiophen and its homologues, contained these substances without anybody being aware of it (*cf.* p. 226).

Nordhausen oil of vitriol is proposed for washing tar-benzols by the Badische Anilin- und Sodafabrik (Ger. Ps. 92018 and 93702). An addition of 4 per cent. of this agent, containing 20 to 25 per cent. free SO_3, is sufficient. This is introduced as a spray into the benzol, kept in agitation, after having first dehydrated the latter by means of ordinary concentrated sulphuric acid (1·84). The apparatus, Fig. 175, consists of a cylindrical case D^3, in which are fixed two concentrical tuyeres D^1 and D^2. Into the inner tuyere D^1 is introduced compressed air or gas, and into the space between D^1 and D^2 the acid to be sprayed. Above the tuyeres the tube D^3 is contracted; the wider orifice F can be closed by cap K; the bottom orifice is

provided with slots E for the passage of the liquid. The apparatus is fixed at the lowest point of a tank filled with tar oil and is started by forcing compressed air or gas through A and D^1, keeping K open, and thus violently pushing the oil upwards through F, other oil entering again at C, so that a circulation is effected. The Nordhausen acid arrives through B, and on contact with the streams of air from D^1 and oil from D^3 it is carried forward, converted into spray and mixed with the oil. When the spraying is finished, K is closed and air is blown in through A and E, to agitate the oil from the bottom.

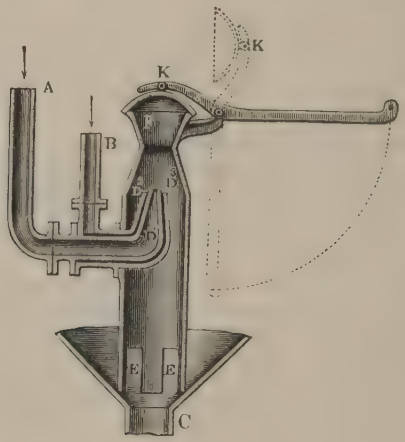


FIG. 175.

This causes the acid-tar to agglomerate, and to settle rapidly after ceasing the agitation. During the settling cap K prevents the acid-tar from getting into D^3 and stopping up the tuyeres. The apparatus is so constructed that the acid-tar cannot stick fast anywhere, but always runs off. In order to avoid losses by the volatility of benzol, this is agitated by itself, by first filling the agitating-vessel to a height of from 3 to 5 feet before forcing in the remaining oil (from an elevated tank) together with the sprayed acid. The acid-tar does not act upon cast-iron blowers or pumps, if the surfaces of the moving parts are protected from moisture by petroleum or lubricating oil where they are in contact with the air. The consumption of Nordhausen acid is

only about half that of ordinary sulphuric acid, the results are better, and the waste of oil smaller. After drawing off the acid-tar, the treatment with water and alkali is performed in the usual manner. This process should not be applied to crude, watery oils, but only as a preliminary to separating the *pure* hydrocarbons.

The washing process described above is probably that generally employed; that is, washing first with alkali, then with sulphuric acid, and again with a little alkali. The employment of the other processes, both those described in our former editions and those now to be mentioned, seems to have been discontinued.

Mansfield used, for every gallon of benzol, ½ lb. of sulphuric acid and one ounce of nitric acid of sp. gr. 1·30, sometimes also a little bleaching-powder and hydrochloric acid. For toluene he took ¾ lb. sulphuric and ¼ lb. nitric acid. For the alkaline treatment he employed lime-water or caustic-soda solution. The less volatile hydrocarbons were boiled for 5 or 6 hours with a quarter of their volume of caustic-soda solution, sp. gr. 1·30, with reflux of the distillate; the liquid was then distilled and purified by dilute sulphuric, nitric, or hydrochloric acid.

Ronalds and Richardson prescribe twice treating with sulphuric acid, mixing for several hours, whereby much heat is evolved (probably by excessive action), washing with water and finally with lime-water or dilute caustic soda. They warn against allowing the light to act upon fresh naphtha, because the water will not readily settle down under the action of light.

Young[1] treats with bleaching-powder, adds dilute hydrochloric acid gradually, and at length caustic-soda solution; the oxidized products collect at the bottom as a black layer, from which the clear oil is easily drawn off. In this way the tar from gas-works in which the richer Scottish cannel coals are used is asserted to be advantageously converted into the ordinary products of the paraffin-oil industry (?).

According to Breitenlohner's experiments with peat-tar oils,[2] the employment of oxidizing agents, as well as lime in lieu of caustic soda, leads to so much inconvenience that, after all, sulphuric acid and caustic soda must eventually be resorted to.

[1] Hofmann's *Report of the Juries*, 1862, p. 140.
[2] *Dingl. polyt. J.*, vol. 157, p. 378.

Locality for carrying out the process.—The mixing-apparatus is best fixed in the same room as the steam-stills with their receivers and the receivers of the benzol-still (see below). Considering the great danger from fire, this building should be constructed without any wood, with an iron roof (for instance, one of corrugated sheet-iron). The roof should be provided with movable ventilators; and the windows ought to possess iron shutters, which can be tightly closed from without with the least possible delay. Open fire (even matches) ought never to be tolerated in this room; it should be lighted by reflectors from without[1] or by electricity. Inside and outside hydrants and hose should be provided, so that every place may be reached by a jet of water. It has been observed that pure water is not very suitable for putting out fires of light tar oils, because these float on the top; but ammonia-water, which is always at hand, does excellent service in this way, probably owing to the volatilization of ammonium carbonate and sulphide;[2] and putting on sand, ashes, and the like acts better than water. The safest plan would be to have one or more pipes leading from the steam-boiler into the room, through which it could be filled with steam by taps or valves *accessible from the outside*; thus the air would be driven out and the fire quenched; but there must be a large volume of steam, and it must issue in several places all over the room.

Treatment of the washed Naphtha.

This can be effected in various ways. Some distil the product at once by steam, as will be described in the next

[1] A case has come under my cognizance, and has been described by me (*Dingl. polyt. J.*, vol. cclix., p. 138), where, in a petroleum-refinery, the vapours issuing from a hot still, after the manhole had been taken off, escaped in such quantity that an explosion was caused by their taking fire on a lamp, burning outside the building, at a distance of 20 ft.; the "flashing" caused the fire to be propagated back into the building, which was completely burnt down.

[2] I noticed this many years ago, also in my German work on tar-distilling, published in 1867 (p. 101). Some time later Mr Watson Smith made the same observation, and strongly recommended the use of gas-liquor (to be stored in close tanks and provided with suitable piping and forcing power) for extinguishing fires in cotton-mills. Strong ammonia liquor has been also recommended for putting out petroleum fires by a Committee of the Munich Polytechnic Society (*Färber-Zeit.*, No. 26, 1882; *J. Soc. Chem. Ind.*, 1882, p. 351).

chapter, and collect the distillates as benzol, solvent naphtha, etc.; others interpose a distillation by direct fire and fractionation. The former process seems at first sight shorter and simpler; but it is advisable only when time presses, since by this plan the last products, especially the burning-naphtha, cannot be kept from discolouring in the course of time. This can be easily prevented by employing the second process, *i.e.*, distilling once more over a direct fire, and making two or three fractions.

This is done in a still exactly like that used for light oil (p. 671); for the sake of cleanliness, it is advisable not to employ the light-oil still itself, but a special *crude-benzol still.* Its worm is made of lead, and, on account of the great volatility of benzol, is rather long. The still and its worm are placed under a shed outside the mixing-house; but the three receivers are either placed inside the house, or at least connected with it by pipes so as to be accessible from within. They consist of well-riveted iron boxes with a manhole and a small hole for running in the distillate from the worm; the latter hole must just fit the pipe, and should be closed by a plug except when in use. This is done both on account of loss by volatilization and of danger from fire, since benzene vapours, even very much diluted with air, take fire most readily.

In firing, the same principle is followed as usual—strong firing during the heating-up, to be moderated immediately when distillation commences. At first the cooling-water is run as fast as a 1-in. water-pipe will permit, so that the distillate runs off quite cold; only towards the end should it run out tepid.

The fractionation is regulated by the thermometer, which is always fixed in the still. This has the drawback that the attendant must be depended upon for changing the receivers at the proper time. But he can be easily controlled by distilling 100 c.c. from a glass retort with thermometer, and noting the quantities passing over at the desired temperatures; according to very many experiments made by the author, the same result is obtained as on the large scale. The volumes thus found are calculated for the quantity put into the still (as measured by an iron gauge-rod in the mixer, or in any other way); and the attendant is instructed to run so many inches depth into each receiver. If there are tables of the contents of each vessel, the

whole, including the calculation, can be done in ten minutes. By this plan a thermometer in the still itself can be dispensed with altogether.

The fixed points of the fractionation will vary according to the desired final products. For 90-per-cent. benzol, the first fraction is made at 110°, the second at 140°, the third at 170°, and the still is then stopped. For 50-per-cent. benzol two fractions suffice, up to 140° and from 140° to 170°. The second fraction, as we shall see, yields next to nothing distilling below 100°, and thus serves only for naphtha. It is not advisable to go beyond 170°, as this would injure the quality of the last naphtha; it is better to allow the still to cool overnight, and to work up the residue eventually, together with light oil, to extract every trace of benzene homologues. The distillation of about 750 gallons lasts 8 or 9 hours, so that a still can be worked off in a winter day; it rarely needs cleaning.

The following table gives some idea of the quantities of the products obtained, in percentages by volume of the raw material:—

	Distillate up to 140° (first product).	Distillate from 140° to 170° (second product).	Residue in the still.
First runnings alone .	60 to 61	15 to 17	20 to 22
Light-oil naphtha . .	30 „ 33	40	...
Mixture of both . .	48 „ 52	22 to 26	...

Utilization of the Waste Acid from washing Tar Oils (Acid-tar).

The specific gravity of the dirty acid, when concentrated oil of vitriol has been used to begin with, is about 1·365; and it generally contains as much acid as corresponds to about 45 per cent. rectified oil of vitrol. It is for the tar-distiller the most troublesome waste product imaginable, killing, as it does, all fish in canals, brooks, and rivers, and is perceptible at great distances by its stench and the red colour of the water. Of course distillers have always incessantly tried to work it up in some way, even without any profit. That this was no easy matter seems proved by the fact that in none of the tar-works visited by me in 1880 had any use been found for this acid, and that it was everywhere allowed to run away or sink into the

ground somehow. In any case, it ought first to be neutralized with lime before doing so. Recently the state of matters has been entirely changed by the uses found for the pyridine bases taken up by the acid-tar; we shall reserve its treatment for this purpose to the close of this chapter, and first deal with the other uses proposed for the acid-tar.

If such tar-acid is diluted with its own bulk of water, most of the impurities rise to the surface as a tough, tarry substance of most disagreeable smell, and can be skimmed off. This substance does not occupy much bulk, and can be got rid of by burying it in the ground or, wherever the sulphurous acid is of no consequence, by burning. It dissolves in alcohol with a fine red colour, but is insoluble in benzene or naphtha. A patent, taken out by W. P. Jenny in Germany (No. 3577), refers to the vitriol-tar from the washing of petroleum; but if it is at all useful, it must also apply to our case. According to one of his methods, the acid is to be diluted with its own bulk of water; the tarry oil precipitated is to be washed several times with boiling water, and at last with a little soda. It is then distilled up to 250°, and the residue in the retort treated for 48 hours with a current of air. The oxygen is absorbed with avidity; and a mass is formed which, after cooling, forms a dark-brown resin. According to the other method, the dirty acid is heated to 100 or 150° for several days, till a sample sinks down in water. It is then poured into water; and the precipitated substance is washed with much water; or else its own bulk of petroleum spirit is first added, in which case the mixture floats at the top. The product is more or less hard, according to its degree of oxidation, and is insoluble in water, alcohol, and alkalis, but soluble in all fats and oils, naphtha, benzene, etc., as well as in the strongest sulphuric acid. Melted up with indiarubber or guttapercha in different proportions, it forms an elastic body which can be used as an insulator; dissolved in light petroleum spirit, it yields a serviceable asphalt varnish.

The dilute acid remaining behind is still red or brown, and disagreeably smelling, as it retains some of the tarry substances, especially all the bases (pyridine, etc.), and sulphonic acids. It has been proposed to employ it for decomposing the phenate of soda (p. 578; but it is not suitable for this purpose, since besides

the colouring-matters, the sulphonic acids and bases would spoil the carbolic acid. It may, however, be used for making superphosphate, and in this case the tarry substances might do some good by protecting roots against insects, etc.; it has been used for this purpose in Scotland. Small quantities might be got rid of by making sulphate of iron or copper.

The Société Oléo-graisse proceeds according to Rave's process.[1] The acid-tar is kneaded with iron, copper, or zinc borings, a little in excess of the quantity required for neutralizing the acids. When that purpose has been effected, the mass is treated with hot water, whereby the sulphates are dissolved and brought to crystallization later on; the melted resins rise to the surface. These, after being well washed with water, have the mechanical properties of soft asphalt. It is rendered harder by heating in a still and collecting the naphtha. The remaining asphalt may serve for many of the purposes of natural asphalt; it resembles indiarubber in elasticity, and is sold as "mineral caoutchouc bitmen." A ton of acid-tar furnishes about 10 cwt. of this purified asphalt. If heated further in a still, until only five-tenths remain, the residue forms a mass almost as hard as ebonite, soluble in naphtha—an excellent insulator for electricity, not acted upon by acids and alkalis, and well adapted for electrical insulation as well as for covering acid-tanks. By interrupting the distillation at intermediate stages, different degrees of hardness can be produced. The heated mass can be pressed into moulds, like papier-mâché. If mixed with 40 per cent. sawdust and a little lime and hot-pressed, an excellent fuel is obtained which burns without melting and with very little ash. On dry distillation, the asphalt is equal to the best coal for the production of gas. By dissolving it in petroleum or naphtha, a good black varnish is obtained which adheres very strongly to metals. When heated in a still, it yields first naphtha, then ($\frac{1}{3}$) light oils, then ($\frac{1}{6}$) heavy oils, similar to the higher paraffins, and in the residue a very hard metallic-looking carbon, which is a good conductor and very suitable for carbon electrodes, etc.

Before Jenny and Rave, Grotowsky had worked the acid-tar from lignite oils for asphalt.

De Grousilliers (Ger. P. 43900) mixes the acid-tar with

[1] Thompson, *J. Soc. Chem. Ind.*, 1888, p. 303.

sufficient sodium or potassium sulphate to form bisulphate; in doing this the impurities separate as a thick tar.

Schwarz and Bauschliger (Ger. P. 46101) expel most of the tar by heating the acid-tar to 150°, allow to cool, add 2 or 3 per cent. of sodium nitrate, and heat slowly to 40° or 80° C. The resinous matters still present are separated as a carbonaceous crust; the acid is freed from nitric acid by heating.

Veith and Schestopal (*Dingl. polyt. J.*, cclxxix., p. 21) mix acid-tar from petroleum with the waste alkali from the same process and with lime, and work the mixture in a black-ash furnace by the Leblanc process, the resinous matter replacing the coal in this process.

Heinrici (*Z. angew. Chem.*, 1898, p. 525) tried to work acid-tar (from lignite oils) for sulphate of alumina or alum, but without economical success. Decolorizing by kieselguhr was not more fortunate. But success was attained by the following process for manufacturing sulphur or pure sulphuric acid. The acid-tar is mixed with $\frac{1}{8}$ of its weight of lignite coke and heated in a retort, whereby all the sulphur is given off as SO_2. The gases are first freed from water by cooling, and then passed through washers charged with heavy paraffin oil, where most of the empyreuma is retained. They are then passed through a stoneware pipe filled with lignite coke, heated to such a temperature that all the SO_2 is reduced to S, but no CS_2 is formed. The sulphur is condensed by cooling, and the CO_2 formed is employed for decomposing the solution of cresote in soda.

Wolniewicz (*Chem. Zeit.*, 1889, p. 1089) dissolves iron, copper, or zinc in the diluted acid, and employs the solution for pickling timber, previously impregnated with resin-soap, whereby metallic resinates are formed.

Ragosine and Dworkowitsch (Ger. P. 43453) convert the acid tar into iron salt, and utilize this, by heating, for sulphurous acid and Nordhausen oil of vitriol.

At Young's paraffin works near Edinburgh the acid-tar was formerly evaporated to dryness and the residue burnt. The sulphuric acid is thus converted into sulphur dioxide, which was utilized in vitriol-chambers. In the great majority of cases no vitriol-chambers are at hand; but the vitriol-tar might still, without dilution (best, perhaps, mixing it with sawdust), be

converted into sulphur dioxide by heating in iron vessels, and that compound be utilized for preparing sulphites or hyposulphites (thiosulphates), or for other purposes.

This proposal (made in the first edition of this work) has been strongly recommended in the *Chem. Zeit.* (1885, p. 777). Attention is there drawn to Roessler's proposal for producing copper sulphate by the action of SO_2 and air upon copper (Ger. P. 22850), and to the employment of SO_2 for decomposing sodium phenate (*cf.* p. 579). For the last-mentioned purpose the empyreumatic substances are to be removed by washing the gas first with water, then with sulphuric acid, and then passing it through cylinders filled with freshly ignited charcoal. A Körting's injector aspirates the gas and forces it through the solution of sodium phenate. After separating the carbolic acid from the solution of sodium sulphate, the latter can be reconverted into caustic soda by boiling with lime, and the calcium sulphite can serve for evolving more sulphurous acid, while the caustic soda is used over again for extracting the carbolic acid from crude carbolic oil. Thus the soda would not be lost, and the loss of carbolic acid, dissolved or suspended in the solution of sodium sulphate or chloride, as formed in the ordinary process, would be equally avoided.

We can here only refer to the paper of Zaloziecki (*Chem. Rev. Fett-Ind.*, 1898, p. 27), who recommends working the acid-tar for aluminium salts, etc.; and that of H. Frasch (*ibid.*, 1898, p. 28), who recovers organic colouring-matters from the same.

Wedge (*J. Soc. Chem. Ind.*, 1899, p. 345) describes the concentration of dilute waste acid from petroleum refining by surface heat, by means of oil-burners.

The most important use of the waste acid, which at some works permits disposing of it entirely to great advantage, is that for making *sulphate of ammonia*. This has been done to a certain extent for a long time past, and I have myself proposed it in the first edition of this work, for the acid previously freed from most of the tar by the addition of water. But this makes the acid inconveniently dilute, and most works consequently decline to practise it. In the raw state the acid cannot be used directly for the manufacture of sulphate of ammonia, because the nauseous tarry substances would make the latter product unsaleable. There is, however, a way out of this difficulty, which has been

utilized at several works for some time, every one of them holding it to be a secret not known to anybody else. By employing vitriol-tar for absorbing ammonia, and carefully skimming off the scum collecting in the ammonia saturators, nearly all the tarry impurities can be removed and a good sulphate obtained. These tarry oils are then worked into the creosote oil or else they are burned; they contain the bases of coal-tar; and these are now to a great extent manufactured in the manner described below.

A very important feature, unknown to most tar-distillers before it was published in a former edition of this work, is the following:—It is well known that sulphuric acid containing any considerable quantity of arsenic cannot very well be used in the manufacture of ammonium sulphate, as arsenious sulphide is formed, which discolours the sulphate. For this reason most English ammonia manufacturers used to employ brimstone-acid, although its price is very much higher than that of pyrites acid. But the latter can be used quite as well, if, during the saturating process a certain quantity of vitriol-tar is added to it. The scum formed from the latter carries the arsenious sulphide up to the top, whence it can be skimmed off, and leaves perfectly white sulphate behind. I have seen this done on a very large manufacturing scale at a Dutch works.

A somewhat similar but much more elaborate process for dealing with vitriol-tar is that patented by the Chemische Fabriks Aktien-Gesellschaft in Hamburg (B. P. 9614, 1885; Ger. Ps. 34957 and 36372), which will be described, p. 699.

The *examination of acid-tar* for alkyl-sulphonic acids, etc., is performed by Heusler[1] as follows:—The acid-tar is diluted with ice-water, neutralized with lime or baryta, and filtered. The filtrate is decomposed by sodium carbonate, and the filtered solution of the sodium sulphonates evaporated to dryness below the boiling-point. The residue, after dehydrating on the water-bath, is heated with aniline on a paraffin-bath during four hours to 170° C., which decomposes the sodium alkyl-*sulphates* with regeneration of the hydrocarbons. These, as well as the aniline, are driven of by steam; from the residual sodium *sulphonates* the hydrocarbons can be regenerated in the usual manner.

[1] *Ber.*, 1895, p. 498.

Recovery of the Pyridine Bases from Acid-tar.

These bases have lately acquired a considerable commercial importance, partly through their employment for the manufacture of colouring matters (*e.g.*, the Ger. P. 105202 of the Höchst Farbwerke for basic diazo-colours), for synthetic purposes and in some other ways, but principally by the fact that the "denaturation" of spirit-of-wine in Germany and several other countries takes place by the addition of these bases.

The properties of the pyridine bases have been described on pp. 230 *et seq.*, and reference to their recovery has been already made in the case of carbolic oil, p. 664. But by far the greatest portion of them is obtained from the acid-tar, obtained in purifying crude benzol, and we therefore describe their recovery in this place.

The pyridine bases can be recovered *immediately from the coal-tar itself*, and although this will hardly ever be done, we will here describe a general method for this purpose.

A large quantity of tar is agitated with a mixture of 1 part of sulphuric acid and 2 parts of water, if necessary, repeatedly. After standing some time the clear liquid is drawn off and boiled in an open vessel, or better in a current of steam, till all mechanically dissolved hydrocarbons have been expelled (along with pyrrol, but, according to some, the pyrrol must have been previously destroyed by the acid treatment). The liquid is now passed through linen cloth, caustic-soda solution in excess added to it, and the whole distilled. The aqueous vapour carries away the bases; if the distillate is not sufficiently concentrated, it is saturated with solid caustic potash, avoiding too much heating; and the oily mixture of bases, separating at the top, is decanted. If it contains aniline, fuming nitric acid is cautiously added and the mixture gradually heated to boiling, whereby the aniline is destroyed; the other bases remain intact. Water is added, the precipitate filtered off, and the filtrate again saturated with caustic potash. The decanted oil contains much water, which is absorbed by solid caustic soda; this should be done completely, since otherwise the boiling-points of the more volatile bases are much changed; and for this purpose the caustic soda must be several times renewed. The oil is now methodically fractionated, sometimes as many as

twenty times, till the boiling-points are constant. The operation is greatly facilitated, and less is lost by decomposition when carrying on the distillations in a vacuum.—Greville Williams destroys aniline and its homologues by heating with potassium nitrite and hydrochloric acid, and then proceeds as above.

The following notes on the isolation of the bases contained in coal-tar are due to a private communication from Dr C. Häussermann. Since there is rarely a sufficient quantity of the mixture of pyridine bases at disposal, which would admit of isolating them by a series of fractional distillations, it is advisable to employ for the preparation of products of constant boiling-points (at least of the lower members of the series) the benzenoid hydrocarbons, isolated by fractional distillation on a manufacturing scale, which are constantly accompanied by those bases. English 50-per-cent. and 90-per-cent. benzol has always been treated at the tar-works with only a small quantity of sulphuric acid, so that it contains both thiophens and bases. Such benzol, after having been fractionated by a Savalle's column into benzene, toluene, and xylene, boiling at a constant temperature, admits the recovery of up to 0·5 per cent. of pure pyridine from toluene, and as much picoline from xylene. If these hydrocarbons are first treated with dilute sulphuric acid, only the bases are extracted, and are at once recovered in the pure state, the fractionation on the large scale having separated the single bases one from another, while thiophen, thiotolen, and thioxen remain behind, and can be extracted by treatment with concentrated sulphuric acid.—Instead of removing aniline from the basic mixture by oxidation, Häussermann prefers to extract it in the shape of aniline sulphate, which is much less soluble than the sulphates of the other bases.

The Chemische Fabriks-Aktien-Gesellschaft in Hamburg (Ger. Ps. 34947 and 36372) combines all these processes also with the utilization of the bases in lignite tar. The tar oils do not contain the bases in the free state; the latter must be first isolated by an alkaline treatment of the oils. The acid-tar is first enriched with bases before being further treated, in the manner following. The acid-tar is diluted with water to sp. gr. 1·2 or 1·25, which causes most of the resinous matters, etc., to separate at the top as a thick tarry layer. The aqueous acid is rendered quite colourless by agitating with crude carbolic acid,

and is then employed for absorbing the bases from crude light oil and carbolic acid, previous to their treatment with concentrated sulphuric acid. The acid solution of the bases is saturated with ammonia in the well-known apparatus for the manufacture of sulphate of ammonia, to be described later on in Chapter XIV. This causes an oily top layer to be formed, containing the bases and the impurities of the acid.

The bases are recovered from this oily layer by distillation. Thus almost the whole of the acid employed for washing the tar oils is recovered as sulphate of ammonia, the bases being obtained casually as a by-product. This makes it pay to employ a great excess of acid, to make sure of absorbing all the bases, and to enrich the bases in the liquid by contact with fresh quantities of oil. The yield of bases from coal-tar does not exceed 0·25 per cent.

Some statements respecting the manufacture of the pyridine bases are made by Scheithauer in his book, *Fabrikation der Mineralole* (Braunschweig, 1895), p. 146. The acid solution, of 15° to 20° Baumé, is freed by long settling from oils floating on the top and resinous matters sinking down, and is filtered through lignite coke with a little cotton-waste. In the clear solution the percentage of pyridine bases is estimated by decomposing it in a graduated cylinder with caustic-soda solution of 38° Baumé. The quantity generally found in liquids from the working-up of lignite is 20 or 30 per cent. crude pyridine bases. The acid liquid is slightly supersaturated with caustic soda or ammonia, the necessary quantity being ascertained by titration. The process is best carried out by placing the soda or ammonia solutions in a vessel and running in the acid solution of pyridine bases *at the bottom*. Thus the bases are separated quickly and in a pure state; the aqueous solution is run off, the bases are dehydrated by a solution of caustic soda of 38° Baumé, and then distilled. The first 75 per cent. are collected, the temperature having risen to 270° C. This distillate is again dehydrated as before, and is separated into the desired fractions by redistillation in a column-apparatus.

Where the manufacture of ammonium salts is not carried on at the same time with the treatment of coal-tar, but the pyridines are to be recovered from the latter, the chemical

washing (*supra*, p. 676 *et seq.*) must be carried out with a view to this. For this purpose, after extracting the phenols from the light oil and crude naphtha by an alkaline treatment, we must treat the oils first with comparatively weak sulphuric acid, say sp. gr. 1·3, in order to extract the pyridines, without a sulphonating action on hydrocarbons, etc. (p. 677). That weak acid may be quite well prepared from the "acid-tar," p. 692, by diluting it with water up to sp. gr. 1·3, by which proceeding so much of the sulphonated compounds, etc., is precipitated that, after a certain time left for their subsidence, the thin acid, although very strongly coloured, can be employed for the absorption of the pyridines.

We shall now describe the usual treatment of the absorbing-acid for pyridine bases, and we commence with the description found in Muspratt-Bunte's *Chemie*, viii., p. 47 (by Kraemer and Spilker).

The crude "pyridine-sulphuric acid" is a brown-red liquid, strongly acid, of sp. gr. 1·2 to 1·3, and contains from 15 to 30 per cent. of bases. The boiling-points of these differ very much, according to the fraction from which they have been obtained, and range from 100° to 200° C. About half of these is pyridines; in the other half, so far, α-picoline, β-picoline, α-α-lutidine, etc., have been found, also aniline and toluidine. Quinoline and its congeners do not occur in sensible quantity in the acid-tar from crude benzol, on account of their high boiling-point (but naturally that will be different with the waste acid from the treatment of the higher-boiling tar oils, in which even acridine, etc., will occur). The most valuable portion are the bases boiling up to 140°, as large quantities of these are required for denaturing spirit-of-wine (in Germany).

Besides the bases, the pyridine acid contains a little benzol and not inconsiderable quantities of rosin-like substances, formed from the tar hydrocarbons, partly dissolved, partly in suspension. These impurities must be removed, as they would pass over into the bases and render these liable to yield turbid solutions. This might be done by concentrating the acid by evaporation and filtering, but it is better done by the process of the Chemische Fabriks-Aktien-Gesellschaft in Hamburg (Ger. Ps. 34947 and 36372), viz., partial precipitation by ammonia, as free as possible from water and H_2S_3, or else by concentrated

gas-liquor, with 20 per cent. NH_3. The treatment takes place in stoneware pots or lead cylinders, provided with two necks at the top, or a neck at the bottom for a tap and a manhole lid. The NH_3 gas is passed in by means of a pipe, reaching to the bottom, and this is continued until a sample of the exit gas smells faintly of pyridine, and the blue reaction on congo paper has just ceased. After a short repose, the contents of the cylinder are found separated in two layers. The top one contains all muddy impurities; the bottom layer is a light-yellow solution of pyridine-ammonium sulphate, and is taken to the vessels where the saturation with NH_3 is completed. Two or three such saturators are combined in such manner that all the NH_3 is utilized, the last remainder being retained in a tower fed with pyridine-acid. Here the treatment is continued until a sample shows a distinctly alkaline reaction with litmus. The ammonium-sulphate liquor settles quickly and well. It is run off by the bottom tap into a separating-vessel, fitted with a partition, where the crude pyridine remains in one compartment and the sulphate liquor flows into the other compartment, from which it goes to the evaporating-boxes, and is in all respects treated like the ordinary ammonium sulphate, as will be described in Chapter XIV.

The crude pyridine is now *distilled* in iron apparatus like the light-oil stills (pp. 671 *et seq.*). The first distillate is treated as "first runnings," until it does not contain more than 10 per cent. water. Then comes a middle fraction, as long as a sample, mixed with its own volume, yields a clear solution, and then the "last runnings," as long as any bases come over. The resinous residue in the still is used as fuel. The last runnings are used as a solvent, or for preparing the higher-boiling bases. The first runnings are dried by means of caustic soda in cone-shaped iron vessels, provided half-way over their bottom with a perforated false bottom, on which is placed the solid caustic soda. The caustic liquor formed collects at the bottom, is drawn off, and is employed for a preliminary drying of another charge of first runnings. The dried oil, together with the middle fraction, is redistilled in an ordinary steam-still such as will be described for benzol (p. 708 *et seq.*), until a sample of the whole distillate yields 90 per cent. at 140°, which is the prescription for denaturing purposes. The small portion

remaining in the still may be collected until it can be rectified by itself, or else it is treated like the last runnings.

Lessing and Wilton (B. P. 4766, of 1905) recover pyridine bases from crude ammoniacal liquor by washing it with heavy tar oil or by washing the exit gases of the ammonia stills, with or without condensation, with a suitable oil, to which preferably a certain quantity of crude cresol is added.

Pure pyridine can be made from the ordinary denaturing mixture by careful fractionating and drying over caustic potash; if needful, interposing a treatment with potassium permanganate. The product should be entirely free from water, give no reaction with permanganate, and yield at least 90 per cent. on distilling between 115° and 118°.

Testing the Pyridine.—A reaction for pyridine, by means of α-dinitro-chlorbenzone, is indicated by Vongerichten (*Ber.*, 1899, p. 2571). Other reactions for distinguishing pyridine from other bases are given by Holde (*Chem. Centr.*, 1902, ii., p. 146) and Bräutigam (*ibid.*, p. 166).

Barthe (*Bull. Soc. Chim.*, 1905, p. 659; *Chem. Centr.*, 1905, ii., 259) declares that pure pyridine does *not* turn red litmus blue, as stated in the text-books. He purifies it from ammonia by means of crystals of $MgHPO_4$.

Milbauer and Stanek (*Z. anal. Chem.*, 1904, 215; *Chem. Centr.*, 1904, i., 1538) treat of the *quantitative estimation of pyridine bases* in the presence of ammonia and aliphatic amines. By adding sodium carbonate to the mixture of salts the ammonia and the amines are converted into carbonates, but the pyridine is set free, whereupon it is shaken out with ether and titrated, using Patent Blue V. N. as indicator.

K. E. Schulze[1] employs ferric chloride for *titrating pyridine bases*, all other indicators being useless. Five c.c. of the bases is dissolved in 100 c.c. water, and 1 c.c. of a 5-per-cent. ferric chloride solution is added. Ferric hydrate is separated in a flocculent state, and normal sulphuric acid is cautiously added until the precipitate has just dissolved.

A test for the proportion of pyridines suitable for *denaturing purposes* is their conversion into the cadmium-chloride compound. The bases separated by caustic soda are distilled with the caustic liquor, until the drops coming over do not any

[1] *Ber.*, xx., p. 3391.

more show the task of pyridine. The distillate is mixed with four times its volume of absolute alcohol, measured, and 10 c.c. of the liquid is mixed with 50 c.c. absolute alcohol and 2 c.c. of a concentrated aqueous solution of cadmium chloride. After standing for 24 hours the white crystals which have appeared are collected on a tared filter and dried at 100° C. One hundred parts of these correspond to 46 parts of pyridine bases (Kraemer and Spilker).

The following directions have been issued by the German Federal Council for the qualities to be possessed by the *pyridine bases employed for denaturing spirit of wine* (*alcohol*). The mixture should be colourless or slightly yellow, and contain not more than 10 per cent. water. At 140° C. and 760 mm. pressure 90 per cent. ought to distil over. A later order, of March 9, 1905, indicates 160° C. as the temperature up to which 90 per cent. should distil over; this means a considerably greater facility for manufacturing the bases since now the lutidines and collidines are useable as well. It should be miscible with water in all proportions without essential turbidity, and free from ammonia. After standing for some time the colour ought not to be deeper than that of a mixture of 2 c.c. normal iodine solution + 98 c.c. water. Ten c.c. of an aqueous 1 per cent. solution, on being shaken with 5 c.c. of a 5 per cent. solution of cadmium chloride, should within 10 minutes yield a distinctly crystalline white precipitate. Ten c.c. of the 1 per cent. solution should give a white precipitate with 5 c.c. of Nessler's reagent. Twenty c.c. of the basic mixture, combined with 40 c.c. of water, should separate no oil-drops. On shaking 20 c.c. of the bases with 20 c.c. of caustic-soda solution, sp. gr. 1·4, and settling, the mixture should yield at least 18·5 c.c. of bases. One c.c. dissolved in 10 c.c. water should not require less than 9·5 c.c. of normal sulphuric acid, until a drop causes a distinctly blue margin on congo-red paper, which soon vanishes.

According to the directions given above, the 20 c.c. denaturing mixture, on being mixed with its own volume of caustic-soda solution, sp. gr. 1·4, should yield 18·5 c.c. of bases and correspond to 9 per cent. of water. In order to estimate the percentage of water more exactly, shake 100 c.c. of the bases in a stoppered 150 c.c. cylinder with fused caustic potash, in pieces of the size of peas, until after thorough settling the

volume of the top layer does not any more decrease and the bottom layer shows a considerable quantity of undissolved potash. Read off at the same temperature as the bases had before the operation, the diminution of volume then indicates the percentage of water.

A test for denatured spirits in drinking-brandy has been indicated by the experts of the German Exchequer as follows:— Evaporate 1 litre of brandy with 1 c.c. concentrated sulphuric acid down to 15 c.c., and add 3 g. solid caustic potash; if pyridine be present, its smell will be perceived at once or after gentle heating. Another test (*Chem. Ind.*, 1900, p. 25) is potassic-mercurous iodide, which in aqueous solutions gives a yellowish crystalline precipitate with pyridine. Before applying this last, the alcohol must be removed by distillation after adding sulphuric acid. The residue is neutralized with caustic potash, and distilled; the distillate is tested as above. The crystals then formed should give the smell of pyridine when heated with caustic potash.

Statistical.—The consumption of pyridines for denaturing alcohol in Germany was in 1899-1900 327 tons, in 1900-1 391 tons, in 1902-3 436 tons, a great part of which had to be imported from abroad.

Quite recently the use of pyridine bases for denaturing alcohol has also been sanctioned in the United States (*Asph. and Teerind. Zeit.*, 1907, p. 68). They are to be employed in the proportion of 0·5 parts, together with 2 parts methylic alcohol, on 100 spirits. The quality of the bases is to be tested as in the German prescriptions.

New Employments of Pyridine Bases.

The Berliner Holzkontor, in 1900, applied for three patents for preparations of pyridine for disinfecting and preserving purposes (Ger. Ps., appl. B25537, 26664, 26665).

According to Merck's *Jahresber.*, 1902, p. 144, pyridine, in dilutions of 1:750 and 1:350, kills Bacterium coli. It is medicinally employed as a solvent for uric acid, against dipsomania, against whooping-cough, for protecting animals against horse-flies.

Wohl (Ger. P. 139669) promotes the esterification of cellulose

by acetyl chloride by the addition of pyridine and quinoline bases.

The Farbenfabriken vorm. Bayer (Ger. P. 145238) convert nitroanthraquinone by heating with pyridine into oxyanthraquinone.

Synthetic indigo is purified by means of pyridine (Hödister Farbwerke, Ger. P. 134139; Compagnie Parisienne des Couleurs d'Aniline, Fr. P. 314681).

Pyridine forms extremely reactive compounds with carbonyl chloride, according to several patents taken out in 1900, 1901, and so on.

Kahlenberg (*Z. angew. Chem.*, 1901, 148) applies it in the preparation of lithion.

Trachmann (*Pharm. Zeit.*, 1902, 470) proposed employing pyridine for taking the CS_2 out of coal-gas. Bueb reports on experiments made with this process as having been unsuccessful (*J. Gasbeleucht.*, 1903, 736).

Fritz Frank (*ibid.*, p. 491) recommends for the same purpose a special mixture containing high-boiling tar bases with benzol, a little aniline, and a little free sulphur.

Quinoline is the starting-point for a synthesis of indigo by the Comp. Paris. des Couleurs d'Aniline (Fr. P. 314681). Decher and Kopp (*Ber.*, 1906, 72) for this purpose oxidize its addition-product with chloro-acetic ester by heating with permanganate, filtering, adding alkali, evaporating, and heating to 200° (*Chem. Centr.*, 1906, i., 672).

CHAPTER XI

WORKING-UP THE LIGHT NAPHTHA INTO FINAL PRODUCTS

THE last rectification of light coal-tar oils is always effected by means of *steam*, either indirectly applied (dry steam) or blown directly into the liquid. In the latter case the steam carries away a large amount of substances boiling at a higher temperature than its own (according to the principles explained, p. 362); and it is hence reserved for the last stage, after the indirect steam has exhausted its action. As a rule, the steam-stills are adapted to either. They also always possess some arrangement for partial condensation or dephlegmation, in order to effect a better separation of the final products.

The steam ought to have a tension of at least 2½ atmospheres, preferably more. It should be, if not exactly superheated, at least completely dried—*e.g.*, by passing it through a coil of pipes, or through a long and shallow iron box, surrounded by the waste heat of the boiler-fire. The tension in the steam-boiler itself must, of course, be higher than the above, preferably at least 5 atmospheres.

The apparatus employed for this final distillation varies greatly. Smaller factories use stills with simple dephlegmators in the shape of worms or tubes. Larger works employ column apparatus, which admit of obtaining the final products without repeated distillation of the intermediate fractions.

The final products of general trade, into which the total crude benzol should be split up without residues, are the following:—

	Furnishes distillate per cent. up to					Spec.
	100°	120°	130°	160°	200°	grav.
90-per-cent. benzol .	90	...	...	...	...	0·885
50-per-cent. benzol .	50	90	...	...	...	0·880
Solvent naphtha .	...	...	20	90	...	0·875
Heavy naphtha .	...	...	...	...	90	0·880

Since for the purpose of manufacturing artificial colours, for other synthetic and for various general purposes a large demand for the *pure* hydrocarbons has sprung up, these now also form one of the branches of many tar-distilleries; but many of these leave that final treatment to their customers and stop at the *commercial* products just mentioned, the manufacture of which we shall describe in the first instance.

English Steam-Stills.

We shall first sketch two different systems of steam-stills, the principal parts of which may be mutually exchanged, so that the dephlegmator of the second system can be attached to the first still, and so on.

Fig. 176, p. 710, shows a system found in operation at large English tar-works. *a* is the still, made of boiler-plate, cylindrical with flat bottom and convex top; *b b* is a wrought-iron jacket round the sides and bottom; *c*, a non-conducting casing of some sort for preventing the loss of heat; *d* and *e* are steam-cocks, *d* supplying the steam-jacket, *e* the perforated coil *f* inside the still; *g* is a self-acting water-injector for the coil *f*. The pipe *h* serves for feeding the still with crude benzol, *i* for discharging the residue, *k* for carrying away the vapours. The latter pipe communicates by the tap *l* directly with the worm, placed outside the still-house, or else, when *l* is shut and *m* is opened, first with the dephlegmator or "condenser" *n n*, made of lead or iron tubes. The latter is placed in the water-filled vessel *o*. The liquid condensing in *n n* collects in *p*, and flows through the vessel *q* and the hydraulic lute *r* back into the still. *q* sends a branch into the main vapour-pipe; but the bends of the pipes prevent the vapours from passing directly from *a* into *q* and thus into the worm. Through the steam-pipe *s* the water in *o* can be heated at will, this being regulated by the thermometer *t*. *u* is the bottom end of the worm, returning into the still-house.

In the second system (Fig. 177, p. 711, the similar or analogous parts being denoted by the same letters as in Fig. 176), *a* is the still, indirectly heated by steam entering through the steam-cock *d*, which communicates with a leaden or wrought-iron coil *b* with water-ejector *g*. Direct steam can be blown in

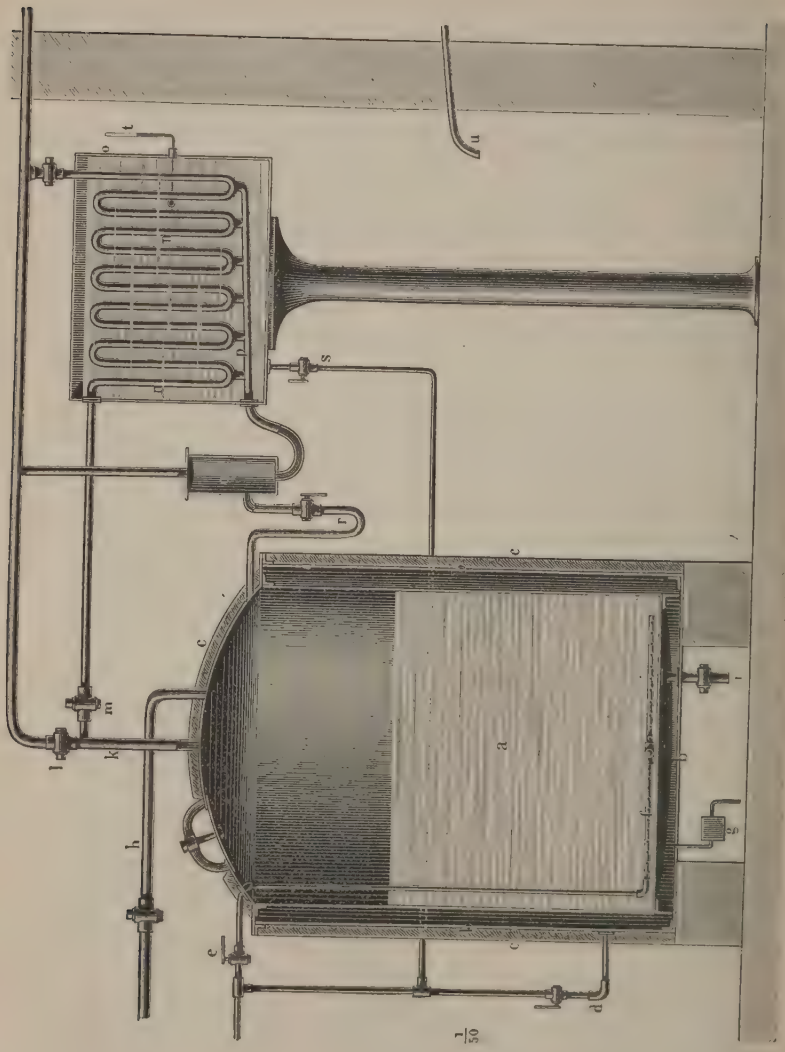
through the cock *e* and the perforated cross of pipes *f*. *h* is the feed-pipe, *i* the delivery-cock, *k* the still-head. To carry the vapours away at once, the cock *l* is opened, when they first pass through the box *v* (for retaining any liquid carried over mechanically—a contrivance which should never be absent), and then enter the worm *w*, made of 1½-inch lead pipe, whose end at *u* returns into the still-house, where also the receivers are placed. The worm-tub is fed with water by *x*; at *y* the hot water runs off. If the vapours are to be dephlegmated, the tap *l* is closed and *m* opened. The vapours then enter the condenser *n n*, whose lower drum communicates with the upper one by fifty copper pipes of ⅝-inch bore. The condensed oil returns into the still by the hydraulic lute *r*; *s* is the steam-pipe for *o*, *t* the thermometer.

The second system appears to be superior to the first. Internal heating by a steam-coil is quicker and attended by less loss of heat than heating by a steam-jacket; and the dephlegmator represented in Fig. 177 especially acts more thoroughly, and impedes the passage of the vapours less than that shown in Fig. 176. Either is preferable to a simple worm, in which the ascending vapours are sometimes stopped by the backflow of condensing oils. Some manufacturers employ proper rectification-columns, as will be described later on in connection with Savalle's apparatus.

C. Lührig (Ger. P. 26679) patents a zigzag pipe, enclosed in another of a similar kind; the cooling water runs in the annular space opposite the course of the vapours; at each downward bend of the pipe there is a branch pipe for taking away the condensed liquor.

C. A. Burghardt employs an inner cylinder, built up of tubes, *a* separated by perforated plates *b* (Fig. 178, p. 712), made of wire-gauze, which, being of greater diameter than the condenser, have their outer rims cooled by the water in the outer cylinder *c*. The vapours pass in at *d*, and are drawn through the apparatus by connecting the upper part at *e* with a draught. The condensed liquid flows by means of the tubes *f* and *g* into the receiver *h*. If this condenser is erected horizontally, the liquid condensing between the single plates *b b* can be drawn off in different states of purity (cf. *J. Soc. Chem. Ind.*, 1885, p. 475).

Another condenser has been patented by L. & C. Stein-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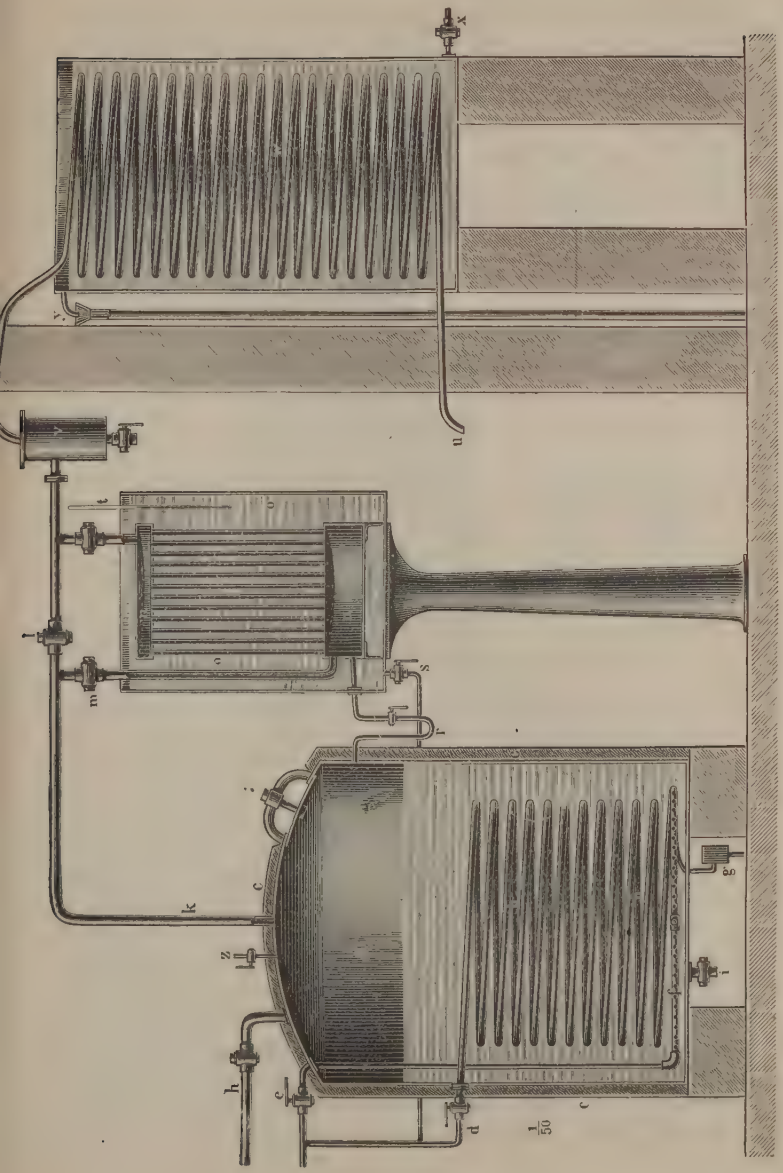


FIG. 177.

müller (Ger. P. 31238); it consists of a series of tubes running parallel to each other in a horizontal direction, and cooled by a number of water-jets along their whole length.

Working the Stills.—The steam-stills are charged with washed naphtha either by means of a pump or an air-pressure apparatus, or else from a store-tank placed in an elevated position, into which the naphtha has first been pumped. Meanwhile the air-vent (seen at *z* in Fig. 177) is opened (it is either a tap or simply a 1-inch aperture), and afterwards closed by a

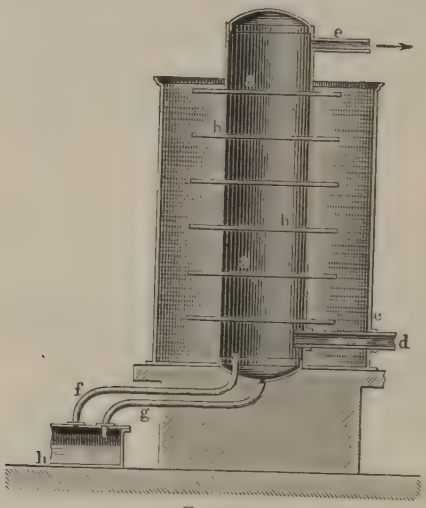


FIG. 178.

cork or a screw-plug. Through this hole an iron gauge-rod can be introduced, in order to ascertain the level of the liquid in the still. The manhole is only opened at longer intervals, for cleaning the still.

It is the rule to pump first the most volatile products into the still, and work them by indirect (dry) steam, then the less volatile products, which are first treated by indirect and afterwards by direct steam. If two products have been made in the benzol-still (p. 692), they are worked separately—viz., the second at once with direct steam, which can be done in a special still fitted merely with an arrangement for blowing in

open steam; the distillation of the first product we shall now describe.

Steam is admitted with full force through the tap *d* into the steam-jacket or the steam-coil *b* (the letters refer both to Figs. 176 and 177). As soon as the liquid begins to boil and to distil, the steam-cock is almost closed, and is then regulated so that the distillation goes on continuously but not too quickly, not to say tempestuously; otherwise there would be loss by incomplete condensation and also danger of fire. At first a little water comes over, which often makes the benzol quite turbid; but this need not be minded, as the benzol soon clears up, either in the receiver or in the store-tanks. Later on, when direct steam has to be used, of course very much water appears, which must be separated from the naphtha. This can be done by the apparatus shown in Fig. 179, for instance, which at the same time permits the naphtha to be finally purified by dilute caustic-acid solution. Two open cylinders of tin-plate, *a* and *b*, 9 inches wide and 2 feet high, are each provided at the top with a channel, serving as a water-lute, into which a tin cover is put; they are connected by the two pipes *c* and *d*, which can be quickly joined or separated by the screw-cap *e*; *c* ends open 1 inch below the top of *a*; *d* bends down inside *b*, and ends just above its bottom. From the bottom of *a* the pipe *f* rises up, passes out and leads to a waste-pipe; it can be shut off by *g*. From *b* the pipe *h* takes away any liquid just below the top, *g* and *e* must leave *a* exactly at the same level; *h* may be at the same or at a slightly lower level. At *i* the end of the cooling-worm is sketched.

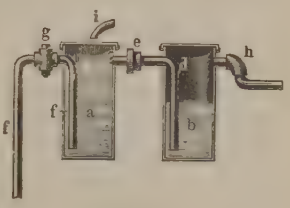


FIG. 179.

Before starting, *a* is three-quarters filled with water. As soon as the mixture of naphtha and water comes out of *i*, *a* is quickly filled up to the level of *c* and *f*, and its contents run out of these two pipes; but as water and naphtha instantly separate, only naphtha will run away from the top (through *c*), and only water from the bottom (through *f*). If *f* were below *c*, the former would fill entirely and act as a siphon, which should not take place. For use in case of need the tap *g* is provided; but this should never be required.

From *c*, the naphtha runs over into *b*, fills this vessel, and runs away into the receivers through *h*. At the last stage, *b* is half filled with dilute caustic-soda solution (sp. gr. 1·10), so that the naphtha must pass through it; why, we shall see later on.

At least *two receivers* are needed; these suffice, if the distillates are run or pumped straight from them into store-tanks; but some distillers prefer receiving the distillates in a large number of smaller drums, which facilitates the classing of the products. Instead of closed iron tanks, open vessels with loose covers are preferable as receivers, since these can be easily inspected and cleaned after each operation, so as to ensure that the final products are quite pure and colourless. In this case, since iron would rust quickly and the water would cause a red mud to be formed, wooden boxes lined with zinc or lead are employed, with their bottom sloping a little to one side, and a tap fixed at the lowest point, so as to draw off their contents completely, either into a store-tank or by means of a pump.

The usual process for separating the distillates is as follows:—First, as above mentioned, only indirect steam is admitted through the top *d* (Figs. 176 or 177). The most volatile products escape first; but from the first, along with benzene, a little toluene also distils, and later on much more, which is unavoidable in any fractional distillation, as explained, p. 363. But since in trade specific qualities of commercial "benzol" are required, means must be sought for obtaining these as directly as possible, with the least possible quantity of intermediate products to be worked over again. For this purpose the principle of *partially condensing the vapours*, with reflux of the condensate into the still, is always employed, as was done long ago by Mansfield; this is the same as has long been known in spirit-distilling as "*dephlegmation*." It is effected by the condenser *n n*, in the vessel *o*. By closing the tap *l* and opening *m*, the vapours arriving by *k* are compelled to enter *n n*, the water in *o* being heated by the steam-pipe *s* to the required temperature. For 90-per-cent. benzol the water-bath should be kept at 60°, for 50-per-cent. benzol at 70° to 80°; but these temperatures cannot be absolutely fixed beforehand, and must be found out by experience for each apparatus; in any case they should be kept as constant as possible. The

liquor condensing in *n n* returns through *r* into the still *a*; it is essentially toluene, with a little benzene. Some manufacturers allow it to run back into *a* directly and continuously (Fig. 177); others interpose a small intermediate vessel (*q*, Fig. 176), if the shape of the condensers makes its more advisable to allow the vapours given off in *g* to get into the main delivery-pipe. Others run the condensate from *n* into a separate closed receiver, in order to rectify it separately. The uncondensed vapours of benzene, with a little toluene, now enter the main vapour-delivery pipe, then the worm *w*; and the benzol condensed therein runs through *u* and the separating-cans, Fig. 179, into the receivers.

After some time, nothing further will come out of *u*; and now the temperature in *o* should be raised to obtain weaker benzol. Usually it is possible, even for making pure toluene, to work with water in *o*, heating it to boiling-point. Water is all the more applicable, if only 30- or 40-per-cent. benzol is to be made at this stage, which is the rule. At most tar-works, in the further distillation no separation into pure hydrocarbons is aimed at, and hence the dephlegmation is not carried further. When nothing more runs from the worm *w*, the condenser *n* is put out of work by closing the tap *m* and opening *l*. Now all vapours pass directly into *w* and are condensed, so that again a considerable quantity of distillate is obtained. Gradually this ceases; and when little or nothing comes over, the indirect steam from *d* is stopped and direct steam is injected through *e* and the apertures of *f*. Even with steam of only 2½ or 3 atmospheres an ample quantity of xylene, trimethylbenzenes, and some tetramethylbenzenes is carried over, which mixture we shall subsequently describe as solvent and burning-naphtha. Xylene is now employed as such in the manufacture of colours, and is for this purpose separated in Savalle's column-apparatus (see below).

We must now see on what principles the *fractionation* takes place. It seems the simplest course to be guided by the thermometer in the still or in the dephlegmator; but as the first requirement is to obtain products fulfilling certain commercial tests, and it is not very easy to carry this out by means of the thermometer alone, other matters must be taken into account. We shall first describe the process carried on at

a tar-works possessing a still with rectifying-column, and working chiefly by the thermometer. Distillation by steam is there performed *twice*. In the first distillation the following fractions are made:—

1st, up to 103° (thermometer in the still), yields 65- to 70-per-cent. benzol.
2nd, 103° to 110°, yields 30-per-cent. benzol.
3rd, 110° to 130°, yields nothing at 100°, 60 per cent. at 120°.
4th, above 130°, yields solvent naphtha.

In the second distillation the dephlegmator has the principal work to do. By rectifying fraction 1 and keeping the dephlegmator at 56°, 90-per-cent. benzol is obtained; with the dephlegmator at 80°, 50-per-cent. benzol comes out. The thermometer in the still, as long as 90-per-cent. benzol comes, never exceeds 100°. When this temperature is obtained, fraction 2 of the first distillation is run in, and the temperature in the still is allowed to rise to 105°, that of the dephlegmator to 80°; the receiver is also changed, and 54-per-cent. benzol obtained. Now the receiver is changed again, open steam is injected into the still, and the distillate collected as solvent naphtha. It would be quite possible in the same apparatus to make pure toluene.

Other manufacturers are not guided by the temperature in the still, but only by that of the dephlegmator; and this seems preferable. It is certain that after some experiments with any special apparatus, and conducting the previous operations on the same plan, the regulation of the temperature of the dephlegmator will by itself permit any desired product to be obtained; *e.g.*, it will be possible to manage so that the whole distillate, when it is mixed up, shall yield 50-per-cent. benzol. The receiver will then be charged for the first time when nothing further passes through the dephlegmator, for the second time when indirect steam does not yield anything even after shutting off the dephlegmator; so that a third product is to be obtained by open steam.

None of these marks can be implicitly trusted to furnish products fulfilling distinct commercial requirements. Hence during the operations several laboratory tests must be made; and some manufacturers depend entirely upon these. The

testing is done in a glass retort, or, better, in a fractionating-flask with Liebig's condenser (Fig. 169, p. 675), taking as fixed points for the fractions only 100° and 120°, and for the later distillates also 130° and 100°.

Silbermann (Ger. P. 186876) describes an apparatus for the *self-acting control of fractional distillations.* The distillates run through a vessel in which a hydrometer is floating which, as its position is influenced by the varying density of the distillates, sets adjustable electricable contacts in motion. These serve on the one hand for opening the communication with the receivers intended to take the distillates of a certain density, and on the other hand for closing the communication with the receiver for the distillate of the next lower density; they also give an optical or acoustical sign in the laboratory or office. Special arrangements are provided for removing the hydrometer without interfering with the taps already closed.

In most cases a previous laboratory test of the charge in the steam-still will give an approximate idea how much of each fraction may be expected. The description and tables given by Davis (*cf.* later on) are intended to indicate beforehand how much of the different products can be run from the still. In accordance with this, a sample is taken a short time before it is thought the receiver will have to be changed, after well mixing up its contents. Supposing *90-per-cent. benzol* to be aimed at, if the test shows that the contents of the receiver just give 90 per cent. at 100°, of course the receiver must be immediately changed, since it cannot be expected that this strength will remain for any length of time if the distillation be continued. Properly speaking, the distillate should always be rather stronger than necessary before being pumped into the store-tanks, to make quite sure of its being sufficiently strong for the purpose intended. Before being pumped away, its height in the receiver is gauged, and the volume (to be ascertained by a table) and analysis are noted. It must now be brought to exactly the proper strength by adding a calculated quantity of the contents of the next receiver. Supposing this to be found = 70-per-cent. benzol, its contents will have to be divided among the store-tanks for 90- and 50-per-cent. benzol. The calculation is made in the following manner:—Supposing 120 galls. of 95-per-cent. benzol to have been pumped from the first receiver, and 160

galls. of 73-per-cent. benzol to be found in the second, the question is, how much of the latter must we pump to the former in order to obtain a commercial product of 90 per cent.? We shall learn this from the proportion :—

$$120 \times 95 + x \times 75 = (120 + x)90$$
$$120(95 - 90) = x(90 - 75)$$
$$x = \frac{120 \times 5}{15} = 40.$$

That is to say, to the 120 galls. of 95 per cent. another 40 galls. of 75 per cent. should be added, to obtain 120 + 40 galls. of 90 per cent. The remaining 120 galls. of 75-per-cent. benzol are pumped into the store-tank for 50-per-cent. benzol, and both quantity and quality noted. Suppose now that the third receiver is found to contain, say, 144 galls. of 40-per-cent. benzol. We shall then put :—

$$120 \times 75 + 144 \times 40 = (120 + 144)x$$
$$x = \frac{14760}{264} = 55.9.$$

This means, if the whole contents of the third receiver be pumped to the 12 galls. of 750 per cent., the mixture will still be 56-per-cent. benzol, and will bear an addition from the contents of the next receiver. But the examples already given will suffice to show how the calculation is made for this or any similar case. Frequently the benzol in the tanks is kept rather above the standard, and is only brought down just before it is sent out; but care should be taken to do this invariably with the immediately following, not with any later fraction.

If no 90-per-cent. benzol at all is required, all the above-mentioned distillates would be pumped into the tank for 50-per-cent. benzol, always noting both quantity and quality. By multiplying each time the number of gallons by the percentage, and dividing the product by the total number of gallons, the percentage of the mixture will be found. The "percentage" in this case is no doubt only an apparent one; a 50-per-cent. benzol has no analogy with a 50-per-cent. solution of a salt or with 50-per-cent. spirit-of-wine; but practice has shown that calculations like those exemplified are quite trustworthy. As a rule they make the product appear slightly below its actual strength; but this is a fault of which the buyer will not

complain, and which the tar-distiller might easily correct if he cared to do so. In the case of important contracts, of course, such calculations will not be depended upon, but the mixture must be specially tested.

Hohenhausen[1] gives the following examples:—500 galls. of crude Yorkshire naphtha which before separation tested

At 110°	120°	130°
16	34	47 per cent.

yielded, as the first portion, with dry steam 250 galls. 40-per-cent. benzol, testing

At 95°	100°	110°	120°
15	39	75	89 per cent.

Wigan crude naphtha, treated in the same way, tested:—

Sample A.	At 110°	120°	130°	140°	150°
500 gallons crude .	17	38	49	58	69 per cent.

	At 95°	100°	110°	120°
200 gallons obtained by dry steam .	14	38	73	89 per cent.

Sample B.	At 110°	120°	130°	140°	150°
500 gallons crude .	13	34	47	57	68 per cent.

	At 95°	100°	110°	120°
200 gallons obtained by dry steam .	15	40	74	90 per cent.

Besides 90- and 50-per-cent. benzol, frequently 40- or even 30-per-cent. benzol is required in trade. What now comes is mostly toluene, and is sometimes sold as such. Commercial *toluol* ought to yield 90 per cent. at 120°. But the next fraction after benzol is sometimes destined for *carburetting-naphtha*. According to a specification proposed by Dr Letheby and adopted by several gas-works, such naphtha ought to yield at least 70 per cent. at 130° and 90 per cent. at 150°; its specific gravity ought to be 0·85 to 0·87. In practice, only the first point need be taken care of; the others will follow of course. This product essentially consists of *xylene*. The specific gravity proves the absence of any adulteration with petroleum spirit. When passing from benzol to carburetting-naphtha, half-filling the second separating-can (*b*, Fig. 179, p. 713) with weak caustic-soda solution should not be omitted. If there is no sale for this

[1] *J. Soc. Chem. Ind.*, 1884, p. 74.

product, it is redistilled and split up into benzol and solvent naphtha.

According to a table given in Wurtz's *Dictionnaire de Chimie* (i., 1663), French distillers would seem to fractionate in a different manner. The first principal fraction received consists of the tar oils boiling from 30° to 150°. They are first redistilled in boilers of 2000 litres capacity by open fire or steam; two-thirds are distilled off, and the residual third run to the second fraction, viz., the oil boiling between 150° and 200° (*cf.* light oil, p. 670). The above two-thirds are treated with acid and alkali, and rectified afterwards, the following fractions being made:—

a. Boiling from 30° to 70°, pentane, hexane, etc.
b. „ „ 70° to 100°, benzene and toluene.
c. „ „ 110° to 127°, "solvent naphtha" No. I. for removing grease.
d. „ „ 127 to 140, "solvent naphtha" No. II. for removing grease.
e. Residue, goes to the second principal fraction.

But it is not possible to separate the hydrocarbons so easily and completely as indicated by Wurtz. None of the tar-works known to the author proceed in this way.

That which follows the weakest benzol, or the toluol, is received as *solvent naphtha;* and some manufacturers make no further fraction, but add to this also everything obtainable from the liquid by direct steam. The name is derived from the fact that this product is used for dissolving indiarubber in the manufacture of waterproof fabrics. It is being extensively employed in the manufacture of anthracene (p. 486), and it also serves for removing grease-spots. It consists principally of xylenes and trimethylbenzenes, no doubt also of other bodies not well understood. The indiarubber manufacturers require the solvent naphtha to be entirely free from naphthalene, which may occur in small quantity in the last distillate by steam. Hence distillation should not be carried too far, but should be interrupted when the product yields 90 per cent. at 150 (some allow 160), and its specific gravity does not exceed 0·875 at 15. This will be the case with the whole as soon as a sample of the distillate, as it flows from the worm, shows 0·880 at 15. Since differences in temperature cause very important differences in the specific gravity, it should never be neglected to reduce the

observed to the normal temperature (which can be done by means of the table in the Appendix).

Solvent naphtha ought to have no very strong and disagreeable *smell;* this is not indicated by the sulphuric-acid reaction, as pointed out by Weger (*Z. angew. Chem.*, 1909, p. 341).

If special stipulations are made for the delivery of solvent naphtha, and if, on the other hand, there is a sale for *heavy* or *burning-naphtha,* the last distillate is received as such. The operation is carried on up to the point at which the distillate begins to show a little colour. Then the steam is stopped at once, and the operation finished. If the washing has been well done, the distillate remains colourless, and the end of the distillation must be judged of by other tests. Smell is a very distinct and characteristic test, but necessarily subjective; naphthalene especially will thus be detected. Another criterion (in this case a certain one) is the specific gravity, which should be 0·900 for the last sample running out of the worm, or 0·880 to 0·887 for the whole of the naphtha; a further test is obtained by shaking up the naphtha: only opalescent beads, instantly vanishing, ought to be formed, and no remaining froth. Moreover, it should not be discoloured when exposed to the sunlight for several days; it will then keep colourless in the dark for a long time.

The distillation of the 5- to 8-per-cent. burning-naphtha which can be got from the distillate up to 140° C. of the benzol-still (p. 716) takes a comparatively very long time. Hence it is often preferred not to distil it at all up to this point, but to mix the residue remaining after getting out the solvent naphtha with the fraction from the benzol-still boiling from 140° to 170°, which is distilled at once by open steam, and yields merely solvent and burning-naphtha.

In all distillations by open steam the box for catching any liquid carried over (*v*, in Fig. 177) is essential for protecting the distillate from discoloration; it should be emptied at least once every day; the caustic liquor in *b*, Fig. 179, must also be renewed daily.

From the product distilled up to 140° may be expected 60 or 76 per cent. of 50-per-cent. benzol, 20 or 25 per cent. of carburetting and solvent naphtha, 5 to 8 per cent. of burning-naphtha. The product distilled between 140° and 170° yields

25 to 50 per cent. best naphtha, 25 to 50 per cent. burning-naphtha, and 25 per cent. residue in the still, which it is best to pass through the light-oil still, although it generally sinks in water.

Apparatus for a Complete Separation of the Naphtha into Pure Benzene, Toluene, Xylene, etc.

Most tar-distillers make only 90- or 50-per-cent., sometimes 40- or 30-per-cent. benzol, solvent and burning-naphtha. Only exceptionally, and that mostly at the colour-works, is a complete separation into benzene, toluene, xylene, etc., aimed at. This can be effected by more perfect apparatus than those hitherto described, carrying out the principle of dephlegmation as completely, as this has long been done in the rectification of spirit-of-wine. Mansfield proposed this already in 1847; but it seems that Coupier, in 1863, first carried it out for the purpose of isolating each of the hydrocarbons in a nearly pure state.[1] His apparatus is shown in Fig. 180, on a scale on 1 : 50. A designates the lower reservoir (the still proper), to which is attached a steam-pipe (forming a coil inside), a manhole, a discharge-cock, etc. B is the opening for feeding with crude benzol. The still is surmounted by the cast-iron rectification-column N, which will be described in detail below. The thermometer *t* is required for regulating the process. The heat of the steam-coil in A (the steam should be at a pressure of 2 atmospheres, or even more for the highest homologues) causes the liquid to boil. In the column N the least volatile oils are condensed by the cooling action of the air and run back into A. The more volatile vapours pass into the trough D, where they are kept at such a temperature that the hydrocarbons of lowest boiling-point remains in a state of vapour, whilst all the higher-boiling ones condense and flow back into the still. For this purpose the vapours pass through the annular spaces of the condensers, placed alongside one another, whose walls are washed inside and outside by the liquid contained in D. If only benzene and toluene are to be separated in the pure state, the liquid in D may be water; for the temperature in D should be kept (by means of the steam-coil

[1] *Bull. Soc. Ind. Mulhouse*, 1866, p. 260; *Dingl. polyt. J.*, clxxx., p. 385.

m and the thermometer *t*) at 60° to 70° for benzene (boiling-point 80°·5) and at 100° for toluene (boiling-point 111°). If

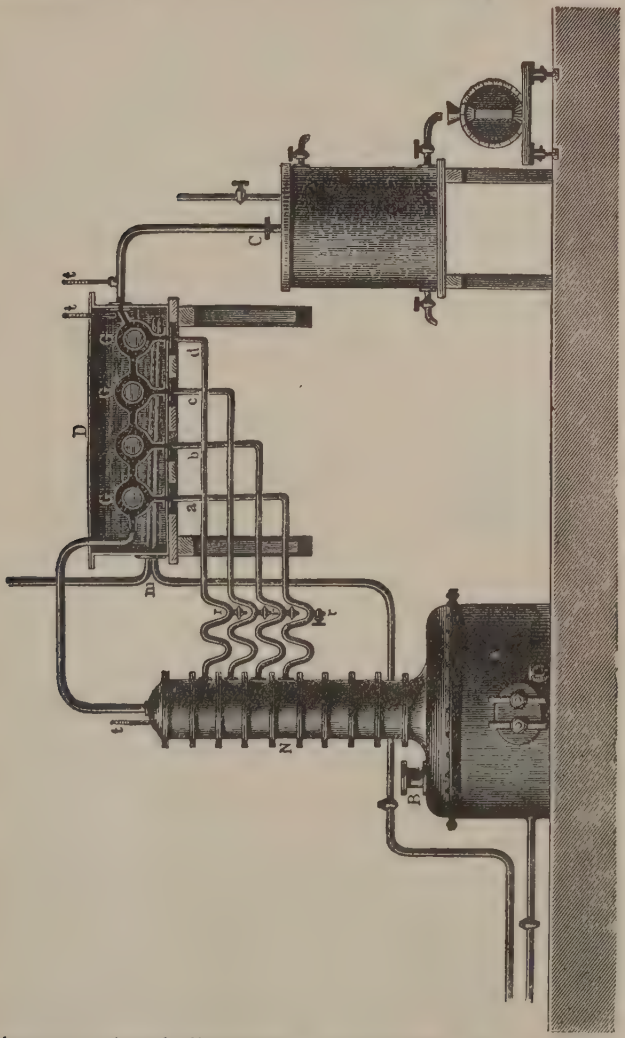


FIG. 180.

xylene or trimethylbenzenes are required, D would have to be filled with a solution of ammonium nitrate (boiling at 164°)

or with paraffin.[1] What condenses in the annular condenser G G runs back to N, through the pipes *a*, *b*, *c*, *d*, whose bends prevent the passage of vapours from N to G G. It will be seen that the liquid first condensed enters the column at a lower place than that condensed afterwards. The taps *r r* serve for taking samples and testing the operation. The vapours issuing from the last condenser pass into the worm C, where they are completely condensed. If crude benzol is distilled, the water in D is first kept at 60° or 70°. When no more benzene comes out of C, the receiver is changed, and the temperature in D raised to 100°. At first a little of a mixture comes over; but soon pure toluene appears, which requires steam of $3\frac{1}{2}$ atmos-

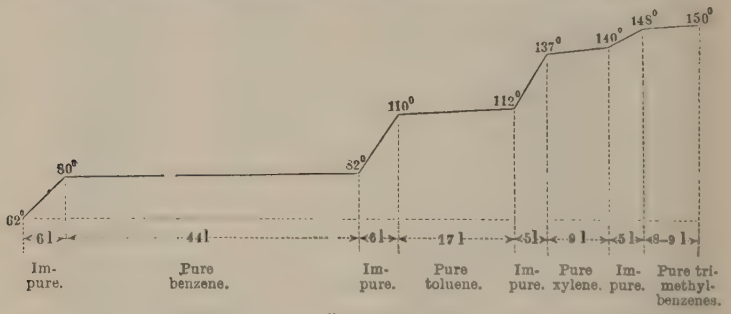


FIG. 181.

pheres in A. When this ceases, the operation is usually stopped; but in case of need, xylenes and trimethylbenzenes can be isolated in a similar manner. Coupier has shown by the above graphical diagram the quantity of principal and intermediate products obtained by his apparatus from 100 litres of crude benzol, boiling from 62° to 150° (say ordinary commercial 50-per-cent. benzol).

Hence 44 litres pure benzene and 17 pure toluene are obtained, and also:—(*a*) 6 litres first runnings, consisting partly of carbon bisulphide, amylene, etc., which may be utilized by adding it to the solvent naphtha; (*b*) 6 litres of an intermediate product between benzene and toluene, which is redistilled; (*c*) about 27 litres high-boiling products, which

[1] This would require steam of 6 to 7 atmospheres for the steam-coil in A; it is hardly ever done.

formerly went at once into the solvent naphtha, but from which now the xylene (9 litres) is sometimes separated.

Figs. 182 and 183 show the plan and section of the compartments of the rectifying-column N (Fig. 180, p. 723) on a scale of 1 : 25. The vapours rise in the pipes *q*, but are checked by caps *r*, and must find their way through the apertures and the liquid standing over them. That liquid, consisting of the portion of the vapours condensed by the cooling action of the air, gradually flows through the overflow-tubes *s* from one plate into another. The labyrinth-partitions ("chicanes") *p p* cause the gas to remain in prolonged contact with the liquid, so as to precipitate the less volatile oils from the vapours, and to carry away by the heat of the latter the most volatile constituents of the liquid. The frequent repetition of this process in the 9 or 10 compartments of the column causes the fractionation to

FIG. 182.

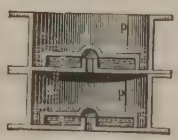


FIG. 183.

be much more thorough than even repeated rectifications without them would have made it.

The "analyzer" of Coupier's apparatus (G G, Fig. 180) would no doubt be advantageously replaced by a more efficient apparatus. This is aimed at in Vedlé's still, where the "benzene rectifier" consists of four larger copper cylinders, surrounded by water, while the "toluene rectifier" resembles that shown in our Fig. 172 (p. 683) at *n o*, and will be best understood from Fig. 184. The vapours pass from the still-head (rectifying-column) A into the analyzer B (6 feet × 2 feet) by the pipe *a*, and the condensed liquid back into A by the pipe *b*, while the uncondensed vapours pass away through *f* into an ordinary worm or condenser of any other form. The vessel B is separated into three parts by two partitions, connected by 60 copper tubes, *d d*, $1\frac{1}{4}$ inch wide. Water flows through *c* into the lower part of B, thence through *d d* into the upper part and away through *e*. When very little condensate is obtained

through *f*, the supply of water through *c* is stopped, and the contents of B are allowed to reach the boiling-point by the heat of the vapours coming from A. At this stage mostly toluene passes over. When this also ceases to flow, the level of water in B is lowered by successively opening the taps g^1 g^2 g^3 g^4, so that eventually the space in B is altogether filled with steam

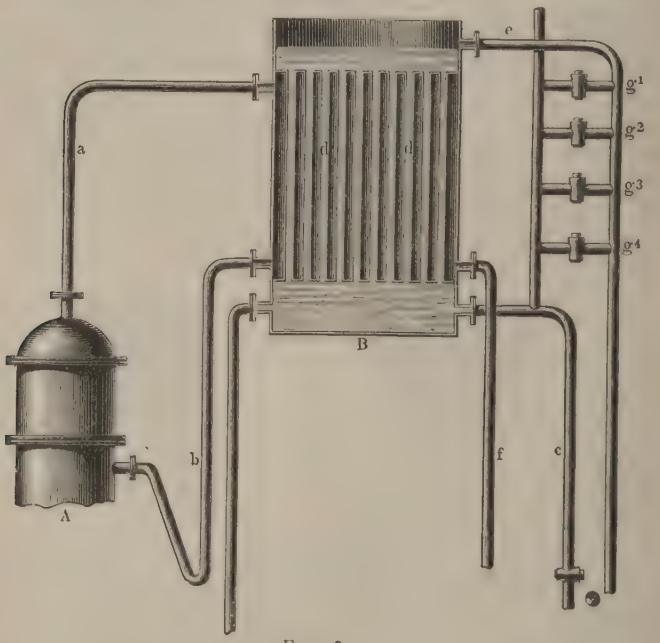


FIG. 184.

inside and with vapours of hydocarbons outside the tubes *d d*. At this stage almost pure xylene passes over.

Egrot's apparatus (mentioned by Hohenhausen[1]) is not essentially different from Coupier's.

The rectifying-apparatus of D. Savalle, fils, of Paris, enjoy special reputation for applicability to the hydrocarbons of coal-tar, and are largely employed by German tar-distillers even for 90- or 50-per-cent. benzol. Figs. 185 to 189 represent this apparatus. In Fig. 185, A is the still, heated by a steam-coil;

[1] *J. Soc. Chem. Ind.*, 1884, p. 76.

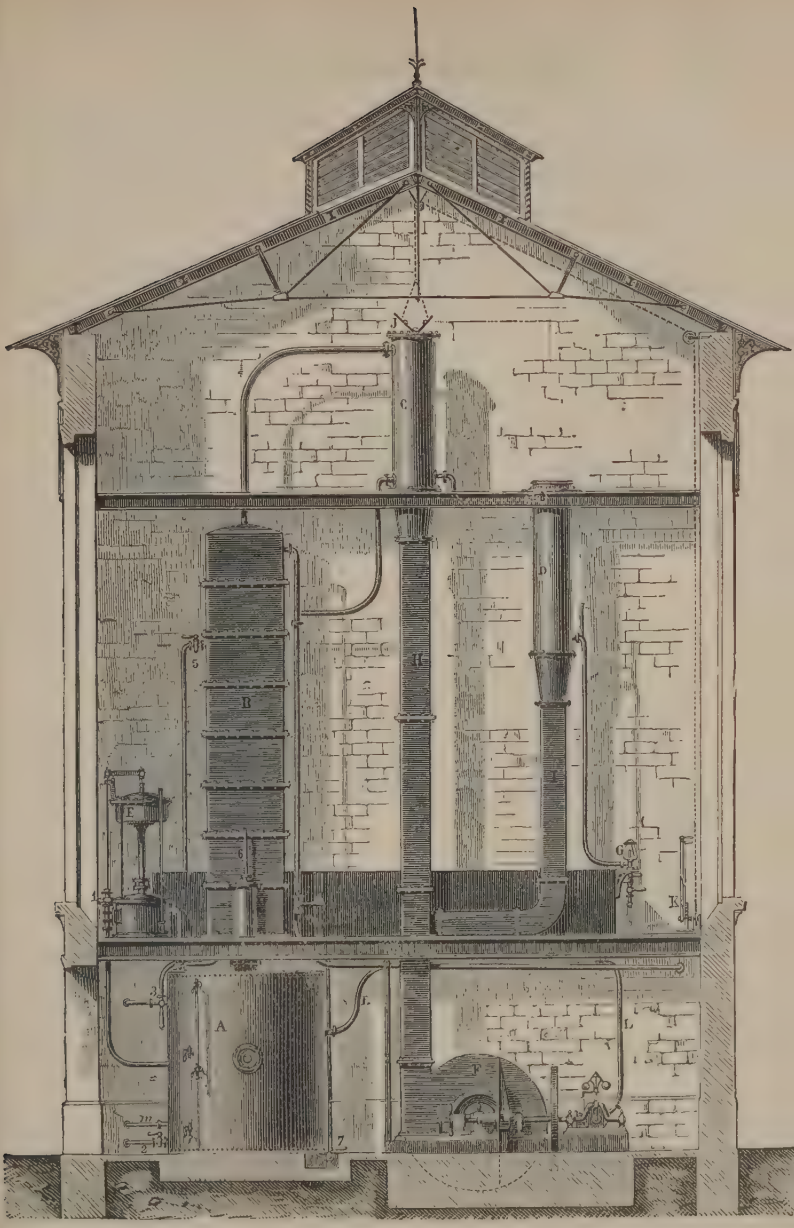


FIG. 185.

B, a square column for the first condensation; C, the air-condenser for the second condensation of the higher-boiling hydrocarbons which are not passed over into the distillate; D, the air-cooler, in which the distillate itself is condensed. The air is supplied by the fan-blast F, through H to C, and through I to D. J is the slide which regulates the current of air in the condenser, by means of a chain and a graduated lever, K. The liquid condensing in D passes through the check-apparatus G,

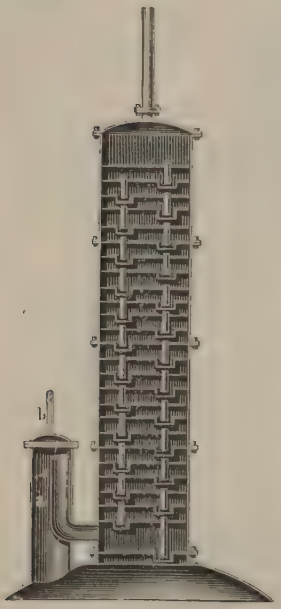


FIG. 186.

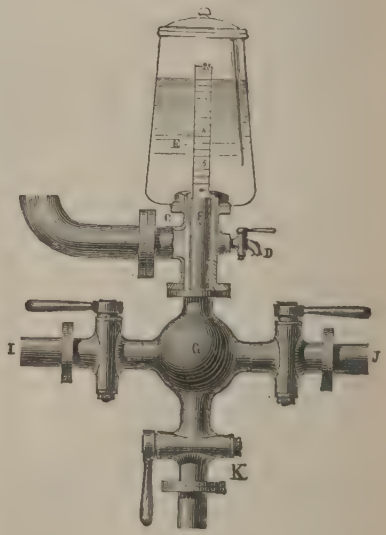


FIG. 187.

for controlling the speed of the distillation. E is a regulator for maintaining a constant pressure in the apparatus throughout the distillation, L is the steam-engine supplying the fan-blast; 1, steam-valve of the regulator; 2, condensed-water ejector; 3, backflow-tap of the column; 4, purifying-tap of the same; 5, discharge-cock of the upper part of the column; 6, thermometer; 7, tap for discharging and charging the still.

The inner arrangement of the column is shown in Fig. 186. The vapours enter it by the cylinder *a*, divided by a vertical

partition into compartments, and provided with a thermometer, *b*. The column is divided into several chambers by horizontal perforated partitions. Each partition contains a perpendicular overflow-pipe which partially dips into a corresponding recess

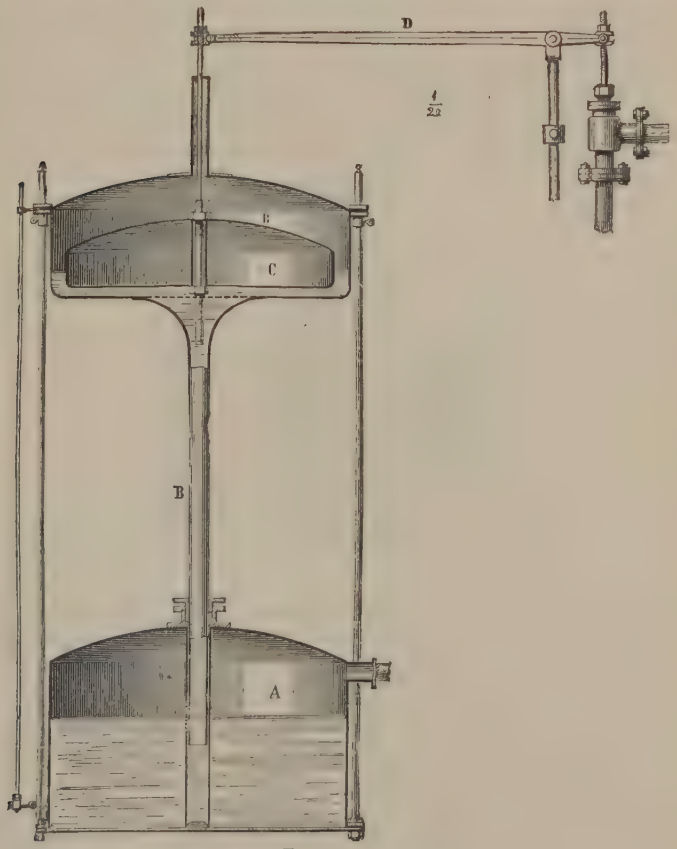


FIG. 188.

of the next lower plate; these overflow-pipes are placed alternately on opposite sides. The higher-boiling products, flowing down the condenser, thus successively pass through all the chambers and finally go back into the column. The perforations of the plates are made of such diameter that the rising

current of vapours prevents the liquid from falling through them, and a depth of about 2 inches of liquid (corresponding to the top of the overflow-pipes) always remains on the partitions: thus the vapours must always pass through the liquid, which considerably promotes the condensation of the higher-boiling products.

Fig. 187 shows the check-apparatus. The distillate from the cooler passes first into the annular space between the pipes C and F. The upper, graduated portion of the latter projects into the glass jar E, and has a small orifice at F. The space

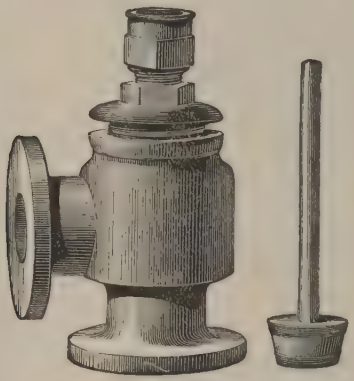


FIG. 189.

between C and F communicates with E. If the flow of the distillate is such that, with the pressure existing in the apparatus, it can run away through the orifice F, the liquid will not rise above this; but if the speed of flow is in excess of that, the liquid will rise from the annular space between C and F into the jar E. This will cause a hydraulic pressure, in consequence of which the distillate will pass more quickly through F. Thus a state of equilibrium will be produced; and it will be seen that the level of the liquid in the jar E, which can be read off on the graduation of F, depends upon the speed of flow of the distillate. Hence, conversely, the latter may be inferred from the former. The size of the orifice in F must of course be regulated once for all on starting the apparatus. The graduation on F is arranged so as to give the quantity of liquid passing hourly through the apparatus; and a glance at it suffices to show whether the

proper quantity of distillate per hour is delivered—that is, whether the apparatus is in order or not. D is a tap for taking samples.

Fig. 188 shows the arrangement of the pressure-regulator. It consists of two superposed vessels connected by a pipe, B. The lower vessel, A, is partly filled with water, and communicates through F (Fig. 187) with the rectifying-column. The upper vessel is provided with a float, C, acting by the lever D upon the conical valve in E. The latter communicates both with the steam-boiler and with the steam-coil heating the still. As soon as pressure is produced in the apparatus, the water must rise in the pipe B, and, when the pressure has attained a certain degree, the water will enter the upper vessel and lift the float C. This depresses the valve E and checks the supply of steam. If by some accident, such as choking up, the pressure in the still should rise too high, the regulator will shut off the steam entirely. By suitable adjustment it can be managed so that, in consequence of the action of the regulator, a certain pressure is never exceeded, which is important both for obtaining a constant product and for preventing accident.

Fig. 189 shows the steam-valve, moved by the regulator.

Further details on Savalle's apparatus for rectifying spirit will be found in the Bulletin de la Société d'Encouragement, 1876, p. 657 (*Dingl. polyt. J.*, ccxxiii., p. 615), and in a pamphlet by Désiré Savalle, "Appareils et Procédés nouveaux de Distillation" (Paris, G. Masson, 1876, 223 pages and 48 diagrams).

The original Savalle apparatus is made of copper; but for benzol cast-iron apparatus are frequently employed, and some manufacturers have such apparatus on a similar principle to, but not identical with Savalle's. The air-cooling system originally employed by Savalle for the rectification of spirit-of-wine has been everywhere replaced by water-cooling, as it was not efficient.

Figs. 190 and 191 show the Savalle column as improved by Heckmann (Ger. P. 39557) by the introduction of bell lutes, intended to avoid any drops of liquid being carried upwards with the steam. The plates of this column are not perforated, and are attached to the sides of the column, far apart. They are supposed to effect a saving of 40 per cent. against other

columns. The dephlegmators and condensers are so arranged that the steam is cooled quite evenly right through. For

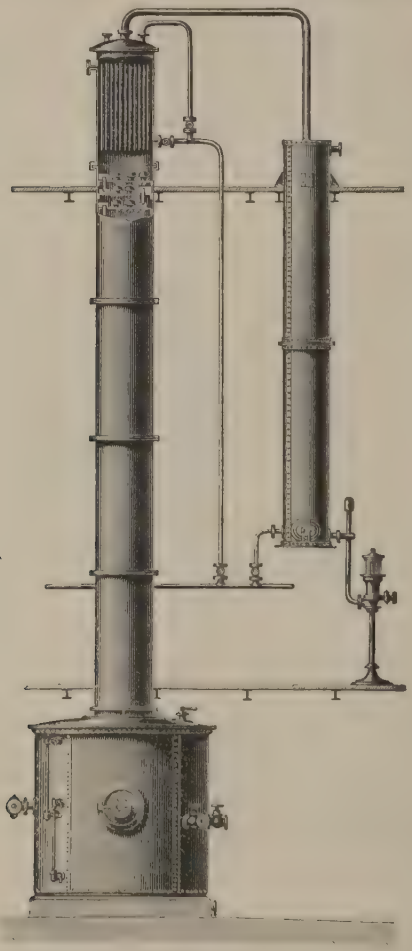


FIG. 190.

benzol, this apparatus is made entirely of iron, inclusive of taps and valves; riveting and soldering is almost entirely avoided; the heating-worms can be taken out in one piece, and all

repairs can be effected without the men having to get inside the still.

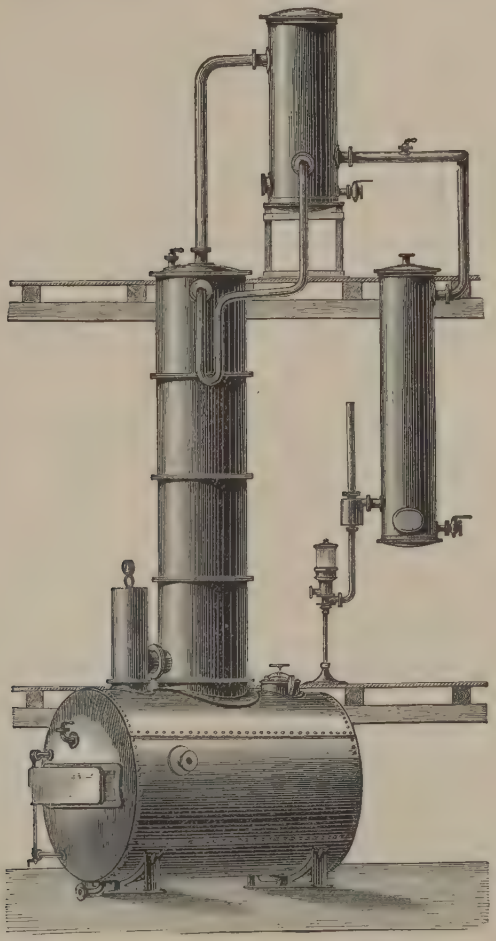


FIG. 191.

Instead of the various intermediate horizontal partitions, shown in the above described apparatus, the column may be filled with conical pots with perforated or fluted sides, placed

over one another, as shown in Fig. 192, so as to break up the current of vapours into many small currents, which suffer innumerable shocks against solid surfaces.

J. H. Miller (B. P. 25469, 1901), describes an apparatus for fractional distillation, containing no rectifying diaphragms, but consisting only of one tube, several metres long, with an inner concentric tube, provided with a great number of holes. There may be two or more columns of this kind combined.

By such columns it is possible to obtain from chemically washed first runnings in one operation commercial 90-per-cent., 50-per-cent., and solvent naphtha. When starting with

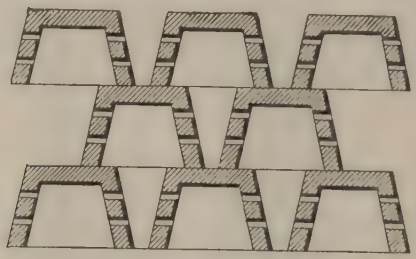


FIG. 192.

50-per-cent. benzol,[1] pure benzene can be obtained, boiling within 0°·5 and completely solidifying in the cold.

Werner and Pfleiderer (Ger. P. 106713) have constructed an apparatus for continuous, automatic fractionation and partial rectification.

Most of the benzol is sold as "90-per-cent. benzol," or benzol No. I. In Germany in 1908 the production of this amounted to about 60,000 tons, half of which is consumed by the manufacturers of artificial colours. The remainder serves for dissolving and extracting purposes in the industry of linoleum and varnishes, and of indiarubber, for removing grease from bones, for carburetting coal-gas and water-gas, as fuel in specially constructed lamps, and for motor-engines, both fixed and in motor cars.

Pure Benzene, Toluene, etc.

The aniline colour-works require almost absolutely pure

[1] Häussermann, *Z. angew. Chem.*, 1892, p. 131.

benzene and toluene, boiling within 0°·3 to 0°·5. These products are mostly prepared at the works, but they are also made by some large tar-distillers, and no doubt will gradually become more general.

Such pure products can be obtained by means of rectifying-columns similar to those described on pp. *722 et seq.*, but even then they contain slight quantities of fatty hydrocarbons, bases, carbon bisulphide, and thiophen, although most of these can be removed as "fore-runnings" from the benzol still. Biehringer (*Dingl. polyt. J.*, cclxxvi., p. 78) found in such fore-runnings 57·3 per cent. CS_2, 7·49 per cent. nitrites, and small quantities of aldehydes and ketones. These, together with thiophens, are removed by repeated treatment with sulphuric acid.

The *carbon bisulphide* (the discovery and quantitative estimation of which in benzol will be described *infra*) seems to have been first found in commercial benzol by Vincent and Delachanal (*Comptes rend.*, vol. 86, p. 340). Most of it occurs in commercial 90-per-cent. benzol, but even in "pure benzene," as it was sold at that time, Liebermann and Seyewetz (*Ber.*, 1891, p. 788) found 0·2 to 0·3 per cent. CS_2 by their own test. Weger (*Z. angew. Chem.*, 1909, p. 339) states that the average contents of carbon disulphide in the great number of samples of 80/81 benzol = 0·1 to 0·2 per cent.

Watson Smith (priv. comm.) has observed in English benzols up to 5 per cent. carbon bisulphide, which gave rise to frequent complaints. The occurrence of this substance is easily accounted for, all conditions for its formation being present in the gas-retorts, viz. red-hot carbon and vapour of sulphur (from the pyrites which always occurs in coal); neither do the ordinary purifying agents, viz., sulphuric acid and alkali, remove it. It is true that a good deal of the carbon bisulphide existing in raw tar will remain uncondensed during the distillation; but some of it must pass into the lightest oils, and more will pass the more perfect the condensing-plant is. Its smell does not betray it, even when 20 per cent. is mixed with benzol, which is much in excess of anything ever occurring in practice. Five per cent. CS_2 in benzol makes no difference whatever in the smell; and even the first distillate smells of benzene, not of CS_2. But a safe test is afforded by the specific gravity, which is much raised by CS_2. Watson Smith, on adding 5

parts of CS_2 to 100 of benzol of sp. gr. 0·875, yielding 20 per cent. below 100°, got on distilling 35 per cent. below 100°, of sp. gr. 0·917. By employing a Linnemann's fractionating apparatus or the like, probably nearly pure CS_2 would have been obtained.

Carbon bisulphide is removed almost entirely in the "first runnings" by careful distillation; the last traces can be kept back by heating with an alcoholic solution of caustic potash and removing the potassium xanthogenate formed thereby by washing. This process answers very well also on the large scale (Kraemer).

Thiophen and its homologues are very troublesome in the manufacture of products from benzol. Bidet[1] found that they cause in nitrobenzene and nitrotoluene a yellow colour, becoming more developed by contact with air. Aniline and toluidine, made from such materials, show the same behaviour, whilst that made from material free from thiophen stands the light and has a much more pleasant smell. Hence aniline-colour makers have every reason to lay stress on the absence of thiophens in coal-tar oils. The tests for it will be described later on.

Even "chemically pure benzene," as understood in trade, contains thiophen. Schwalbe (*Fischer's Jahresber.*, 1906, ii., p. 27) found in the purest commercial benzols 0·01 to 0·04 per cent. sulphur in the form of carbon disulphide and thiophen. *Cf.* also the statements of Weger, p. 735. Pure benzene is made from the article boiling between 80° and 82°, by allowing it to crystallize in a freezing-mixture, and separating the crystals from the mother-liquor by pressing, or by a centrifugal machine. This operation should be repeated once or twice. In order to remove the thiophen, this benzene must be agitated with renewed quantities of strong sulphuric acid till it ceases to give the blue reaction with isatin. Willgerodt[2] asserts that it can be purified by treating with chlorine-water. Haller and Michel[3] obtain benzene quite free from thiophen by boiling it with 0·5 or 1 per cent anhydrous aluminium chloride, washing with soda and distilling. According to Boedtker,[4] in this case H_2S is formed, a molecular condensation of thiophen and benzene taking place to a liquid boiling at

[1] *Monit. scient.*, 1889, p. 487.
[2] *J. pract. Chem.* [3], xxxiii., p. 479.
[3] *Bull. Soc. Chim.* [3], xv., p. 390.
[4] *Comptes rend.*, cxxiii., p. 310.

upwards of 300°. But Heusler[1] ascribes the formation of this liquid to the action of $AlCl_3$ on non-saturated hydrocarbons.

Aluminium chloride, in the manner described above, is commercially employed by the Société anonyme des matières colorantes de St Denis (Ger. P. 79505). The benzene is heated with 0·5 per cent. $AlCl_3$ for several hours, decanted from the tarry matter which subsides on cooling, washed with sodium carbonate, and distilled.

Lippmann and Pollak (*Chem. Centr.*, 1902, ii., p. 737) show that chloride of sulphur at 100° C. does not act upon pure benzene, but all thiophen is removed if the benzol is heated with 15 per cent. sulphur chloride on the water-bath for 192 hours, then distilled by steam, washed with alkali and dried with calcium chloride (such a treatment is evidently too expensive for technical purposes).

Daub (Ger. P. 123053) purifies benzol from sulphur compounds by treating its vapour with carbon monoxide. Witzek (*J. Gasbeleucht.*, 1903, p. 85) points out that thiophen is just very stable at high temperatures! Daub's patent lapsed already after twelve months.

Schwalbe (Ger. P. 133761) removes CS_2 from benzol by moist ammonia gas, and thereupon thiophen by a mixture of sulphuric and nitric acids. The cost is stated = 6d. per 100 kg.

Donath and Ditz (*Chem. Centr.*, 1900, i., 325) state that they remove both CS_2 and thiophen from benzol by treating it with alkaline permanganate solution at a higher temperature; but Russig states that this does not act on thiophen.

Commercial 50-per-cent. benzol sometimes contains 0·1 per cent. *pyridine*, and the toluene made from this 0·25 per cent. pyridine. This, as well as other basic substances, are detected by agitating 100 parts of benzol with 4 parts of 10-per-cent. sulphuric acid for half an hour, separating the acid solution by means of a tap-funnel, making it alkaline with caustic soda, and distilling in a current of steam. The distillate is saturated with nitric acid and evaporated to dryness on a water-bath. Or else, in lieu of distilling, the free bases are extracted from the solution by means of ether. Properly purified benzol ought not to contain anything soluble in dilute sulphuric acid, and but little imparting a dark colour to strong sulphuric acid. Sometimes

[1] *Berl. Ber.*, 1896, ref. p. 656.

a maximum is stipulated for the percentage of substances dissolved out by strong sulphuric acid, viz., non-saturated hydrocarbons and thiophens. The former can also be determined by titration with bromine-water. Nitric acid of sp. gr. 1·4 should not produce any white vapours when poured into benzol, and ought not to colour the benzol on agitating.

Toluene, if present in "chemically pure benzene," is recognized, according to Raikow and Uerkewitch (*Chem. Zeit.*, 1903, p. 295), by nitrating it (*cf.* p. 765) and adding caustic soda to the product at ordinary temperature. Chemically pure nitrobenzene remains colourless, but even a minute quantity of nitrotoluene produces a yellow-brown colour, especially when the product has been diluted with a little gasoline.

Whilst it is possible to manufacture benzene sufficiently pure for the highest requirements of colour-makers by double rectification and additional sulphuric-acid treatment, the case is different with *toluene*, and especially *xylene*. Here paraffins and olefins occur, boiling at the same temperatures as the above, which go along with the nitro- and amido-products, and can be recognized in the latter as a turbidity on dissolving in dilute hydrochloric acid. On the small scale, these fatty hydrocarbons can be removed as resinous matters by boiling with sodium. On the large scale, this is done by agitating with hot sulphuric acid containing nitric acid. Thus the thiophens are destroyed, the olefins polymerized, and the paraffins after nitrification can be blown off by steam. Thus purified toluene and xylene yield much more amides.

According to Witt (*Chem. Ind.*, 1887, p. 9; 1894, p. 31), at the aniline-works 0·5 to 1 per cent. nitric acid is generally added during the last purification of benzol, to destroy cumarone and indene.

Friswell (*Chem. News*, 1893, lxviii., p. 27; *J. Soc. Chem. Ind.*, 1893, p. 589) mentions that recently much toluene from oil-gas tar occurs in trade, containing a large quantity of paraffins, which in toluene are even more injurious than in benzene. They are not indicated by the boiling-points, but by shaking the toluene with the same volume of sulphuric acid, sp. gr. 1·84. In the case of pure toluene the layers separate at once; the acid is colourless or faintly brown, and remains so for 27 hours. With impure toluene, emulsions are formed separating only

after 5 or 10 minutes; the acid takes a bright orange colour, after an hour green at the top, after 24 hours altogether green or black. Whilst it is usual to remove the impurities by strong sulphuric acid or even by Nordhausen oil of vitriol (p. 687), in which case much toluene is converted into sulphonic acid, Friswell recommends on the latter account less concentrated acid, viz., 10 volumes per cent. sulphuric acid, sp. gr. 1·84, to be agitated for four hours; after settling and drawing off the acid, the oil is at once washed with caustic-soda liquor. The loss does not exceed 5 per cent., and consists half of paraffins.[1] Some toluenes require more energetic treatment than others. After washing they are rectified and leave behind polymerized bodies of 260° to 285° boiling-point. The waste acid, in order to be recovered, must be separated by dilution from a dark green oil, which, if almost free from acid, is soluble in water.

Xylol.—The tar-distilleries mostly supply only the mixture of the three isomers, viz., about 60 per cent. metaxylene, 10 to 25 per cent. orthoxylene, and 15 to 30 p.c. paraxylene, with a little ethylbenzol and small quantities of trimethylbenzenes, paraffin, and thioxen. The German Benzol Union demands for "pure xylol" a yield of 90 per cent. within 3°·6 and of 95 per cent. within 4°·5. The reaction with sulphuric acid may be faintly yellow. The sp. gr. of commercial xylol is 0·867; its flash-point at about 21°.

Xylol is employed for preparing nitroxylol and xylidines, and for removing naphthalene obstructions in gas-pipes.

Xylol (*i.e.*, the mixture of the three isomeric xylenes) can be purified in a similar manner to benzene and toluene. Ethylbenzene can be removed, according to Friedel and Crafts (*Comptes rend.*, 1892, cxii., p. 1110) by treating with bromine, 20 times the weight of the oil, and a little iodine, but this of course is not a technical method.

Reuter (*Chem. Zeit.*, 1889, pp. 830 and 850) indicates the following method as applicable to separating the three isomeric xylenes on a large scale. Sulphuric acid of more than 80 per cent. H_2SO_4 acts on metaxylene, but para- and orthoxylene are not acted upon by acid below 84 per cent. If the ordinary

[1] "Paraffins" are not dissolved or changed by sulphuric acid, least of all such of only 1·803; no doubt non-saturated hydrocarbons are meant.

strong acid of 93 to 95 per cent. is employed, metaxylene is acted upon until the proportion of water to real acid attains 20 : 80, but for the other isomers 16 : 84. Hence an acid saturated with metaxylene can receive $\frac{1}{8}$ of its weight of fresh acid without dissolving para- or orthoxylene. The crude xylene (which ought not to boil below 136°, 90 per cent. passing over till 145°) is washed several times with small quantities of sulphuric acid, in cast-iron pans with agitators at 80° C., in which case only metaxylene is converted into sulphonic acid. This is secured by employing just the proper quantity of acid, as found in a preliminary trial made with a kilogram of the xylene. The solution containing 2 or 3 per cent. mechanically dissolved paraffins and terpenes, is freed from these by dilution to 1·4 sp. gr., avoiding a rise of temperature above 100°. After separating the oil rising to the top, the mass is allowed to cool, when most of the α-metaxylenesulphonic acid crystallizes out. From this metaxylene is regenerated by heating at 220° with water in an autoclave, or by dry distillation of the ammonia salt, 80 or 90 per cent. being thus recovered.

From the oils separated from the metaxylenesulphonic acid, the paraxylene is recovered by treating them with an *excess* of sulphuric acid at 80° C., and treating the acid liquid as above described. The paraxylenesulphonic acid is purified by recrystallization, and the hydrocarbon is quantitatively recovered by decomposition with water in the autoclave (dry distillation of the ammonia salt yields only about 20 per cent.).—The orthoxylene remains in the mother-liquor from the paraxylenesulphonic acid, and is obtained by converting the sulphonic acid into the calcium, then into the sodium salt, acidulating this, and treating the free sulphonic acid as in the case of paraxylene.

Somewhat similar to Reuter's process is that of Crafts (*Comptes rend.*, cxiv., p. 1110). Börnstein and Kleemann first convert the xylene mixture into xylidines, and separate these by means of sulphur dioxide, which forms crystalline compounds with ortho- and metaxylene, leaving paraxylene in the liquid state. Of course this process can be thought of only where the xylidines themselves are wanted.

Nearly pure metaxylene, which is sometimes required for technical purposes, can be made by the following process, communicated to me by Dr C. Haussermann. Ordinary xylol,

which contains but little orthoxylene, is first agitated with 5 per cent. of its weight of strong sulphuric acid, in order to remove the thio-compounds, and is then converted into sulphonic acids by agitating with its own weight of sulphuric acid, sp. gr. 1·84, for several hours. The acid solution is separated from the undissolved portion, and is then treated with a current of steam (as indicated by Armstrong for decomposing sulphonic acids). The metaxylene distilling over needs only to be freed from acid, in order to be worked up at once for metaxylidine. All these operations can be carried out on the manufacturing scale without any difficulty.

Levinstein's method for separating the three isomers of xylene in the laboratory for analytical purposes will be described later on.

Composition and Properties of the Commercial Descriptions of Benzol and Naphtha.

The distillation of the products from light tar oils in the laboratory, carried out in the manner described later on in this chapter, yields the following distillates (in percentages by volume), according to my own tests:—

Commercial products.	Initial boiling-point.	88°	93°	100°	110°	120°	130°	138°	149°	160°	171°
90-per-cent. benzol . .	82°	30	65	90	...	...	...	...	...	...	...
50-per-cent. benzol . .	88°	...	13	54	74	90	...	...	...	...	...
Toluol	100°	...	...	...	56	90	...	...	...	...	...
Carburetting-naphtha .	108°	...	...	...	1	35	71	84	97	...	...
Solvent naphtha . .	110°	...	...	...	...	17	57	71	90	...	...
Burning-naphtha . . .	138°	...	...	...	...	...	...	...	30	71·5	89

The temperatures were all measured with the thermometer-bulb just submerged in the liquid, at the beginning of the distillation.

Häussermann[1] quotes the following results:—

At . .	85°	90°	95°	100°	105°	115°	120°	135°	140°	145°	150°	170°	180°
90-per-cent. benzol .	20	72	84	95	95	98	...	...	...	...	...	...	...
50-per-cent. benzol .	...	5	30	50	64	81	94	...	...	...	...	...	...
Solvent naphtha .	...	...	...	...	...	...	...	6	48	72	85	92	95

[1] *Industrie der Theerfarbstoffe*, pp. 13 and 14.

According to another statement, made to me by an English tar-distiller, the ordinary results are :—

At . .	100°	120°	130°	160°	Sp. gr.
90-per-cent. benzol . .	90	...	...	...	0·885
50-per-cent. benzol . .	50	90	...	...	0·880
30-per-cent. benzol . .	30	90	...	...	0·875
Solvent naphtha . . .	...	...	20	90	0·875
Burning-naphtha . . .	...	...	...	30	0·885

Hohenhausen quotes :—

Benzol.					
90-per-cent. Sp. gr. 0·882.		50-per-cent. Sp. gr. 0·878.		30-per-cent. Sp. gr. 0·875.	
	Per cent.		Per cent.		Per cent.
At 83°	5	At 94°	10	At 97°	12
85°	22	95°	18	98°	21
88°	62	98°	40	100°	30
90°	74	100°	50	105°	55
92°	81	105°	68	110°	73
95°	87	110°	79	115°	84
103°	90	115°	85	120°	90
105°	94	120°	90		
110°	98				

Schultz (*cf.* also his results, p. 745) quotes :—

At . .	85°	90°	95°	100°	105°	110°	115°	120°
90-per-cent. benzol .	25	70	83	90	94	97	98	99
50-per-cent. benzol .	0	4	26	50	62	71	82	90
30-per-cent. benzol .	0	2	12	30	42	70	82	90

In Germany recently the "benzols" are designated by Roman numbers, and correspond approximately to the English designations as follows :—

Benzol No. I. to English 90-per-cent. benzol.
„ II. „ 50-per-cent. „
„ III. „ toluol (in Germany : 0-per-cent. benzol).
„ IV. „ carburetting naphtha.
„ V. „ solvent naphtha I. ("Lösebenzol").
„ VI. „ solvent naphtha II. („).

"Heavy benzol" of commerce to burning-naphtha.

The percentages which these various grades yield on distillation are given by Kraemer and Spilker as follows :—

Up to Degree Centigrade per cent.

Benzol. No.	85°	90	95	100	105	110	115	120	125	130	135	140	150	160	170°	180	190
I. . .	48	78	87·5	91·5	...	...	...	...	...	...	...	...	...	...	...	...	...
II. . .	...	3	31·0	52·0	67	77	84	90	...	...	...	...	...	...	...	...	...
III. . .	...	...	...	...	11	49	79	91	95	...	...	...	...	...	...	...	...
IV. . .	...	...	...	...	...	...	...	...	...	30	60	87	...	...	...	...	...
V. . .	...	...	...	...	...	...	...	...	...	...	...	20	75	91	...	...	...
VI. . .	...	...	...	...	...	...	...	...	...	...	...	...	5	50	84	...	...
Heavy benzol	...	...	...	...	...	...	...	...	...	...	...	...	...	...	45	82	91

Besides these types, small quantities of "Cumol" and "Pseudocumole" are found in the German trade, where also the types of "30-per-cent." and "0-per-cent." benzol, understanding by "per cent." the quantities distilling up to 100° C., are found.

Cf. also, *infra* (p. 759), the percentage of pure hydrocarbons and of impurities in these types as found by the same authors.

Quite recently, by the name of "Technisches Benzol," a product is coming into the German market, consisting of about 95 per cent. real benzene + 5 toluene, and yielding on distillation at least 90 per cent. up to 90° C.

Another classification, employed by the German Union of Benzol Manufacturers, is the following one :—

Designation.	Boiling-point (° C.).	Colour.
90-per-cent. crude benzol .	90 to 93 per cent. up to 100° . .	...
Purified 90-per-cent. benzol	90 to 93 per cent. up to 100° . .	Water white.
Purified 50-per-cent. benzol	50 per cent. up to 100°; 90 per cent. up to 120°	Water white.
Pure benzol . . .	90 per cent. within 0°·6; 95 per cent. within 0°·8	Water white.
Crude toluol . . .	90 per cent. between 100° and 120° .	...
Purified toluol . . .	90 per cent. between 100° and 120° .	Water white.
Pure toluol . . .	90 per cent. within 0°·6; 95 per cent. within 0·80° . . .	Water white.
Crude xylol . . .	90 per cent. between 120° and 150° .	Water white to yellowish.
Purified xylol . . .	90 per cent. between 120° and 145° .	Water white.
Pure xylol . . .	90 per cent. within 3°·6; 95 per cent. within 4°·5	Water white.
Crude solvent naphtha .	90 per cent. within 150° and 180° .	...
Purified solvent naphtha, No. I.	Not less than 90 per cent. up to 160°	Water white to faintly yellow.
Purified solvent naphtha, No. II.	Not less than 90 per cent. up to 175°	...
Heavy benzol . . .	Boiling below 200°	...

Allen[1] gives the following results of distilling the commercial products in the usual way :—

	Very good first runnings (once-run naphtha).	Good 90-per-cent. benzol.	Scotch 90-per-cent. benzol.	50/90-per-cent. benzol.	80-per-cent. benzol.	Solvent naphtha.	Mixture of 70 pure benzene and 30 toluene.
Spec. grav. .	...	0·882	0·873	0·880	0·875	0·877	0·880
	Degrees.	Degrees.	Degrees.	Degrees.	Degrees.	Degrees.	Degrees.
First drop collected at	...	82	...	...	...	...	85·4
10 per cent. ,, .	96	83½	84½	94	97	128½	86·6
20 ,, ,, .	99½	84½	85	95	98	130	87·2
30 ,, ,, .	102	85	85⅞	96½	99½	132½	87·8
40 ,, ,, .	107	85⅝	86½	98	101	135	88·8
50 ,, ,, .	111	86⅜	87⅜	100	104	137	89·8
60 ,, ,, .	119	88	89	102½	106	140	91·4
70 ,, ,, .	128	89⅝	91½	106	109½	143½	93·2
80 ,, ,, .	145	92½	94⅝	110½	113½	148½	96·2
90 ,, ,, .	170	...	...	120	120	156	102·6
92 ,, ,, .	...	100	...	...	...	...	...
95 ,, ,, .	...	...	...	...	...	...	107·0

According to the same author, a good sample of 90-*per-cent. benzol* should not begin to distil under 80° and should not yield more than 20 to 30 per cent. at 85°, or much more than 90 per cent. at 100°. An excessive distillate, *e.g.*, 35 to 40 per cent. at 15°, indicates a larger proportion of carbon bisulphide (see below) or light hydrocarbons than is desirable. The actual percentage composition of a 90-per-cent. benzol of good quality is about 70 per cent. of benzene, 24 of toluene, a trace of xylene, and 4 to 6 of carbon bisulphide and light hydrocarbons. It should be colourless and free from opalescence. The specific gravity of English 90-per-cent. benzols usually ranges from 0·880 to 0·888 at 15°·5; that of Scotch benzols (which contain little carbon bisulphide, but a considerable proportion of light hydrocarbons) is often as low as 0·871. 50-90-*per-cent. benzol* is a product of which 50 per cent. by volume distils over at a temperature not exceeding 100°, and 40 per cent. more below 120°. 30-*per-cent. benzol* yields 30 per cent. at 100°, and 60 per cent. more between 100° and 120°; it consists chiefly of toluene and xylene. *Solvent naphtha* gives from 8 to 30 per cent. distillate below 130°, and about 90 below 160°; it consists chiefly

[1] *Commercial Organic Analysis*, 1st ed., vol. ii., p. 87.

of toluene and xylene, with notable quantities of cumene and still higher homologues, and several per cent. of naphthalene [to some of this I must demur; there can be but very little toluene in this product; and "cumene" does not occur in coal-tar at all, but only isomers of this body].

According to Allen,[1] some contract-notes for continental customers specify the following tests for commercial benzol:— 1st, 1 c.c. is agitated with 20 c.c. of pure concentrated sulphuric acid and allowed to stand for some hours. The coloration at the end of this time should be very slight, never exceeding a pale straw-yellow. 2nd, 10 c.c. of the sample is agitated in a stoppered bottle with successive small quantities of saturated bromine-water, until a yellow tint is obtained which remains for some minutes. Not more than 0·5 c.c. of bromine-water should be required to produce this result.

Hohenhausen quotes as usual *specific gravities* of English 30-per-cent. benzol 0·875 at 15°, of 50-per-cent. benzol 0·878, of 90-per-cent. benzol 0·882. When the specific gravity is lower than 0·875, the presence of paraffin or non-nitrifiable hydrocarbons may be suspected. Most of the Scotch benzol has a lower specific gravity, on the average 0·870, and contains 7 or 8 per cent. of paraffins, some of it as low as 0·860 (Trewby).

The following statements give the yield of *pure hydrocarbons* from commercial products.

G. E. Davis[2] finds in 90-per-cent. and 50- to 90-per-cent. benzol:—

	90-per-cent.	50- to 90-per-cent.
Pure benzene . . .	75	50
„ toluene . . .	24	40
„ xylene . . .	1	10

Schultz quotes the following yields, as obtained by a rectifying-column:—

	From 50-per-cent. benzol.	From 90-per-cent. benzol.
Fore-runnings up to 81° . .	5 to 10	10 to 27
Pure benzene	30 „ 40	65 „ 75
Benzol for red	5	10
Pure toluene	35 „ 40	2 „ 4
Xylenes	5 „ 8	

[1] *Comm. Org. Anal.*, 2nd ed., ii., p. 475.
[2] *J. Soc. Chem. Ind.*, 1885, p. 648.

Häussermann (priv. comm.) regularly obtains 70 parts of pure benzene from 100 parts of 90-per-cent., and 45 to 48 pure benzene from 100 parts of 50-per-cent. benzol by means of a Savalle's column.

Cf. also the results of Coupier, p. 724, and of Kraemer and Spilker, p. 758.

The following statements are made by Weger (*Z. angew. Chem.*, 1909, p. 339). "*Pure benzol*" of commerce, also designated as 80 to 81 per cent. or crystallized benzol, has a sp. gr. = 0·885 at 15°, fusing-point = 5°, and boiling-point = 80°·5. According to the rules of the German Benzol Union, of such "pure" benzol, 90 per cent. should pass over within 0°·6, 95 per cent. within 0°·8, and there should be hardly any colour produced by sulphuric acid. Such "pure benzol" still contains thiophen and carbon disulphide, as well as traces of toluol and paraffins. The quantity of thiophen which V. Meyer stated = 0·5 per cent. is in reality only about 0·15 per cent. (For details on this point and on the tests for thiophen, *cf.* Weger, *loc. cit.*) Benzol *free from thiophen* is also manufactured in Germany and sold in truck-loads; it is made by thorough washing with concentrated sulphuric acid. The average percentage of carbon disulphide in "pure benzol" is 0·1 to 0·2 per cent. Generally it is of no importance, but is troublesome in some analytical methods, where it may cause errors. It may be removed from the benzol by treating it with ammonia or with alcoholic potash. "Pure benzol" is employed for preparing nitrobenzene and benzene sulphuric acids, serving for the synthetical production of phenol and resorcin.

Pure toluene of commerce, according to a private communication from Dr Häussermann, ought to satisfy the following tests:—It should boil within 1°. When shaken up for some time with its own volume of strong sulphuric acid, it ought not to cause any coloration. On shaking up for some minutes 90 c.c. of toluene with 10 c.c. of nitric acid of sp. gr. 1·44 in a stoppered jar, the acid should assume only a red colour, and remain quite clear and bright, not turn greenish or blackish and thick. Some samples of toluene which answer to these tests still contain 0·5 per cent. of non-nitrifiable hydrocarbons, which may be troublesome on the large scale; these should be tested

for, as will be described hereafter, but not less than 1 kg. of toluene ought to be employed for this test.

Pure Toluol of commerce has the sp. gr. 0·872 at 15°, boils at 111°, and solidifies only at −90° C. According to the rules of the German Benzol Union, 90 per cent. should distil within 0°·6, 95 per cent. within 0·8, and the sulphuric acid reaction should produce hardly any colour. It contains traces of benzene, xylenes, paraffin, and thiotoluene. The latter is found by Laubenheimer's reaction (blue-green colour with phenanthrene-quinone, glacial-acetic acid, and concentrated sulphuric acid). Toluol free from thiotoluene can be also obtained in commerce.

The ordinary "pure toluol" is employed for the manufacture of trinitrotoluene (as an explosive agent), of toluidine, benzyl chloride, benzaldehyde (for artificial indigo), etc.

Testing Benzol in the Laboratory.

1. *Fractional Distillation.*

A test always performed is that by *fractional distillation.* For this purpose usually ordinary glass retorts or fractionating-bulbs are employed (see Fig. 169, p. 675). In this case the position of the thermometer is of great importance (p. 675), and also in other respects different results may be obtained in apparatus of unequal construction. On this account, and owing to the fragile nature of glass retorts, Regnault, at the instance of the French Government, constructed a *standard apparatus*,[1] which is shown in section in Fig. 193. A is a cylindrical copper retort with a neck, *a*, and a bent vapour-tube, *b c*. The latter fits tightly into the lateral tubule *d* of the condenser B. This consists of a brass cylinder, *e f*, ending at top and bottom in narrow metal tubes, *g* and *i*, and fixed air-tight in a wider metal cylinder, *m n*. Into the latter enters a stream of water through *o* at the bottom and leaves at the top at *p*. It stands on a tripod, P P, to which a horizontal frame, *h l*, is attached. In the latter slides a carrier, V, containing five glass tubes, closed at the bottom and divided into cubic centimetres, each of which can be thus brought under the outlet-pipe (*i*) of the condenser. By means of a pipette the retort is charged with 100 c.c. of oil, which ought not to occupy much

[1] *Ann. Chim. Phys.*, lxviii., p. 409.

more than a third of it. The thermometer T is fixed in the tubule *a* so that its bulb does not dip into the liquid, and that the 80th degree comes out very little above the cork. The distillation is carried on by the gas- or alcohol-flame S. The ordinary fixed points for changing the receivers 1 to 5 are 100°, 120°, 140°, 160°, and 180°. The convenience of this arrangement for changing the receivers and reading off the volume of each

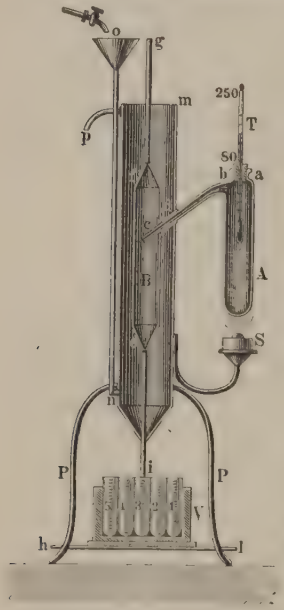


FIG. 193.

FIG. 194.

fraction will be at once apparent. The condenser is cooled by means of water.

Herr (*Chem. Zeit.*, 1908, p. 148; *J. Soc. Chem. Ind.*, 1908, p. 217) describes another kind of dephlegmator. This is a glass tube, 300 to 1000 mm. long, filled with lead shot, six of which weigh 1 grm. The cylinder is covered with cotton-wool or the like, to prevent loss of heat. Further arrangements are described by means of which it is possible to fractionate liquids at temperatures up to 330° C., such as petroleum.

English distilling method.—At the tar-works and at the

buyers' laboratories glass retorts are employed for testing benzol. Frequently differences of opinion occur between buyer and seller, chiefly caused by the fact that it is not usual in the English trade to place the thermometer in the only proper position, as shown in the diagram, Fig. 169, p. 675, but to let it dip more or less into the liquid. Further deviations are caused by differences in the size of the retorts and the speed of the distillation. The following detailed directions by W. W. Staveley[1] are intended to produce a uniform result; but this would involve their being accepted everywhere as binding, which is far from being the case. One hundred c.c. of the sample is to be put into an ordinary 6-oz. stoppered retort, connected with a Liebig's condenser whose condensing-tube is 1 in. wide and 30 ins. long. The thermometer is so fixed that its lowest point is $\frac{3}{8}$ in. from the lowest portion of the retort. Heat is applied by means of a Bunsen rose-burner (Fig. 194), in such a manner that the distillate runs in separate drops into the 100 c.c. burette employed as the receiver. A moment before the desired temperature is reached the lamp is removed, whereupon the thermometer rises to the proper point; and the reading-off is made as soon as the benzol has ceased to drop from the condensing-tube. The contents of the retort, after cooling, are poured into the burette; and the loss, if any, is added to the percentage of the distillate. New corks absorb benzol, and hence are not to be recommended; neither are new clean retorts suitable, unless a few grains of brick are introduced. Best of all are retorts which, having been used for some time, have a slight coating of carbon inside.

Some years ago I found at the largest English tar-works 8-oz. retorts, whose beaks dipped into condensing-tubes $\frac{7}{8}$ in. wide and 27 ins. long, surrounded by a glass cooler, as shown in Fig. 195. The thermometer was so placed in the retort that its end was $\frac{3}{8}$ in. from the bottom.

Allen,[2] in contradiction to many assertions respecting the uncertain results of the ordinary English commercial-benzol testing, asserts that very constant results can be obtained by different operators, the variations rarely exceeding 1 or $1\frac{1}{2}$ per cent. if the test is properly understood. He gives the following

[1] *Chem. News*, xliii., p. 70.
[2] *Comm. Org. Anal.*, 2nd ed., ii., p. 496.

instructions for conducting the ordinary retort-test, so as to ensure results as accurate as the process will admit of. They apply to 90-per-cent. benzol, which must, of course, be modified to suit other qualities. One hundred c.c. of the benzol is measured in an accurately graduated cylinder, and poured thence into a tubulated retort holding 200 c.c., or 8 fluid ounces. A delicate thermometer, 14 ins. long and with a small bulb, is

FIG. 195.

fixed in the tubulure by a cork so as to be vertical, and so that its bottom is $\frac{3}{8}$ in. distant from the bottom of the retort. The first marking or division of the thermometer is at 70°, which point should be well out of the retort, and the graduation should be continued up to 130°, with divisions at each $\frac{1}{2}$°, or better $\frac{1}{5}$°, of a degree Centigrade. Thermometers, otherwise similar, but differing some 6 ins. in the height of the 100° mark, give distinctly different percentages in benzol-testing.[1] The

[1] Proper thermometers are obtainable from L. Casella, 147 Holborn Bars, London, E.C.

neck of the retort is inserted into the inner tube of a Liebig's condenser, and pushed as far as it will go. The condenser should be from 15 to 18 ins. in length, and well supplied with cold water. The neck of the retort should not project too far into it, and, if necessary, should be cut short. No cork or other connection is necessary between the retort-neck and condenser-tube. Before use, both the retort and the condenser should be rinsed with a little of the sample and allowed to drain; or a little benzol is distilled in it and the residue carefully drained out. The graduated cylinder employed for measuring out the sample is next placed (without drying it) under the further end of the condenser-tube in such a manner as to catch all the distillate, while allowing it to drop freely. The retort is then heated by the naked flame of a Bunsen burner, furnished with an air-regulator working automatically with each movement of the tap, and surrounded by a cylinder to exclude currents of air.[1] The flame should be small, about the size and shape of a filbert, and, when the distillation of the benzol commences, must be so regulated that the condensed liquid shall fall rapidly in distinct drops, not in a trickle or a continuous stream.

When the distillation commences, the flame is regulated, if necessary, and the rise of the thermometer carefully watched. The moment it registers 85°, the flame is extinguished. But as the thermometer even then still rises from 0°·5 to 1°·0, this must be allowed for. A little experience shows the amount of this after-rise for each special case; thus, if it be 1°, the gas should be turned out when the thermometer registers 84°·5, because it will still rise to 85°·5, and thus 85°·0 may be considered the mean reading. Four or five minutes are allowed for the liquid in the condenser to drain into the measuring-cylinder, and then the volume of the distillate is carefully read off and recorded. The lamp is then relighted, and the distillation continued till the thermometer rises to 100° (observing the same precaution as to the after-rise), when the gas is turned off as before, and the volume of the distillate is read off, allowing time for drainage. The residual liquid in the retort is allowed to cool, and is then poured, to the last drop, into the measuring-cylinder. A

[1] It is well to place the lamp in a deep tin basin to hold the benzol in the event of a retort cracking.

deficiency from the 100 c.c. originally taken will generally be observed. This deficiency, amounting to 1 c.c. or so, which is supposed to be caused by loss of benzol (although it is due far more to expulsion of acetylene and other gases), is added to the reading for each temperature, and the corrected volumes reported as the "strength" of the benzol examined. The variations in barometric pressure are allowed for by deducting or adding 1° C. for each inch below or above 30 ins. Thus, if the barometer marks 29·5 ins., the gas should be so extinguished that the thermometer may mark a mean temperature of 99°·5 instead of 100°. [According to my observations, this correction does not hold good for elevated situations, where the deviation from 30 ins. is too great; in that case the only practicable way is to distil pure benzene at the same time, and regulate the thermometer accordingly, as will be explained below. Altogether the method just described cannot be considered as accurate in any way.]

An anonymous writer[1] has asserted that for each $\frac{1}{10}$ in. lowering of the barometer 0·8 per cent. more is found than at the normal pressure; but this is evidently exaggerated. W. Thomson[2] recommends immersing the distilling-vessel entirely in a copper water-bath, so that the quantity passing over will be ascertained independently of the shape of the vessel, the state of the barometer, etc.; then the water might be siphoned off, and the copper box used as an air-bath for the higher temperatures. But it is here overlooked that the temperature inside the retort is several degrees below that of the water- or air-bath. In any case the water-bath would have to be brought, by the addition of common salt or the like, to such a temperature as to raise that inside the retort to 100°.

I have myself, in an extended investigation,[3] in which I was aided by contributions from many of the largest producers and consumers of benzol, shown the great uncertainty attaching to all the ordinary testing methods founded on fractional distillation. It was found that the results were influenced by the following circumstances:—the material of the retort (glass or metal); the shape of the same; the presence or absence of a dephlegmator; the exact position of the gas-delivery tube with

[1] *Chem. News*, xliii., p. 93; li, p. 170. [2] *Ibid.*, xliii., p. 115.
[3] *Chem. Ind.*, 1884, p. 150.

reference to the level of the liquid, its width, and the way it was joined to the neck of the flask; the position of the thermometer; the length, width, and inclination of the condenser; the rate of distillation; the mode of reading-off; the barometric pressure. Uniform results can only be obtained by eliminating most or all of these disturbing influences, preferably in the following manner. A quantity of the purest obtainable article is set aside as the "type." The sample to be tested is distilled in any suitable apparatus, the more rationally constructed the better, and immediately before or after a similar quantity of the "type" is distilled in the same apparatus exactly in the same way.

The above investigations were continued by a special committee of the German Society of Chemical Industry, whose report has been made by Dr Bannow.[1] There was an extraordinary diversity of opinion which ultimately led to the conclusion that different classes of substances, as alcohols, phenols, hydrocarbons, bases, etc., behaved differently with regard to their boiling-points, and that hence uniform rules for determining boiling-points can hardly be established. Bannow himself (the manager of Kahlbaum's works) employs for the most heterogeneous substances a globular retort of a capacity of 200 c.c. (say, 7 ozs.), made of platinum, silver, or copper, 0·7 mm. (= $\frac{1}{36}$ in.) thick, and 73 mm. (= about 3 ins.) diameter, consisting of two flanged halves screwed together and made tight with a ring of wetted or oiled cardboard. [This arrangement has the drawback that the joint between the two half-globes is not always tight.] On the top there is a neck, 1 in. long and $\frac{3}{4}$ in. wide, provided with a glass still-head, $\frac{1}{2}$ in. wide outside and 4 ins. long, with a globular enlargement in the centre, and $\frac{3}{8}$ above this a side-tube, branching off nearly at a right angle, sealed on without any contraction. The still rests on asbestos cardboard, with a circular hole of $1\frac{1}{4}$ ins. diameter, and is heated by a plain Bunsen burner, whose flame always burns blue. The cooler is 800 mm. (= 31 ins.) long, and inclined at such an angle that the outlet is 4 ins. below the inlet. The thermometer is made of thin glass, not thicker than half the width of the glass still-head; the mercury-bulb is placed in the centre of the globular enlargement. The

[1] *Chem. Ind.*, 1886, p. 328.

thermometer-scale can be moved up and down by means of an adjusting-screw. The charge is 100 c.c.; the 3 c.c. first distilling are rejected, and the distillation is carried on so that 5 c.c. per minute, or 2 drops per second, pass over. It is continued till the receiver has been filled up to 100 c.c. No correction is made for barometric pressure; but the thermometer-scale is adjusted by means of the screw before every test, by distilling 100 c.c. of a normal "type" and fixing the scale in the moment when 60 c.c. have passed over.—Most of these points were adopted by the other members of the commission; but they all objected to the use of metal retorts, preferring glass, and to the rejection of the first and last portions of the distillate [which, in point of fact, is not possible in benzol-testing].

Mendelejeff[1] employed, for the testing of Caucasian petroleum, a special method, consisting in conducting the vapours issuing from the dephlegmator of the first retort through a tube which passes down to the bottom of the second retort, and from there through a dephlegmator of the same contrivance into a third, fourth, and fifth retort. When the temperature of the last retort has reached the height desired, the distillation is discontinued, and only resumed after the contents of the first retort have absorbed the contents of the remaining ones. Thus a very great number of fractions were obtained.

Forel[2] employs a glass flask, A (Fig. 196), holding 200 c.c. The glass tube B, 60 cm. long and 18 mm. bore, is connected by tube *a* with the Liebig cooler D, 80 cm. long. The thermometer C is divided from 0° to 100° in $\frac{1}{5}$°, and the mercury is entirely surrounded by the benzol vapour. One hundred c.c. are distilled off always in the same space of time (16 to 17 minutes) and at the same barometric pressure of 738 mm. [how is that to be secured?]. At this pressure, water boils at 99·2°; benzene boils with 734 mm. at 79°, with 738 mm. at 79·2°, and with 743 mm. at 79°·4. For each 20 degrees of the thermometer not surrounded by vapour, 1° must be added.

The method now to be described, as published by F. Frank in *Chem. Ind.*, 1901, p. 240, and in Kraemer and Spilker, in Muspratt-Stohmann's *Chemie*, vol. viii., p. 34, has been worked

[1] *J. Soc. Chem. Ind.* 1883, p. 371. [2] *Chem. Zeit.*, 1897, p. 393.

out on the basis of the conditions laid down by me in 1884 (p. 752), and is an amplification of the prescription given by Bannow (p. 753). It has been adopted by the leading German benzol manufacturers as the standard method.

1. The still, *a*, Figs. 197 and 198, is made of sheet copper, 0·6 to 0·7 mm. thick, of a globular shape, 66 mm. diameter, with a neck for receiving the thermometer tube 25 mm. long, 20 mm. wide at the bottom, and 22 mm. at the top.

2. The thermometer tube, *b*, is of glass, 150 mm. long, 14 mm. wide inside, with a bulb 30 mm. wide, midway of its height. The side-tube, 8 mm. wide, is joined to it 10 mm. above the bulb, nearly at a right angle.

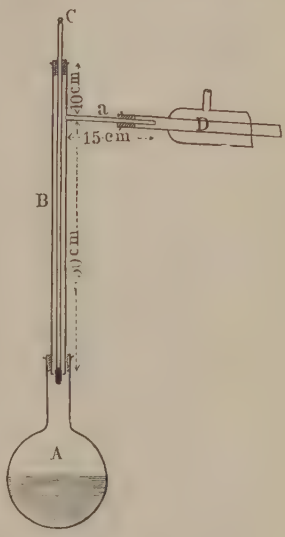


FIG. 196.

3. The still stands on an asbestos slab, *c*, provided with a circular hole, 50 mm. diameter. The furnace, *d*, has four round holes, 10 mm. below the top, for the escape of the products of combustion. The heating is performed by an ordinary Bunsen burner, *e*, 7 mm. wide, whose flame must be blue at any position of the tap.

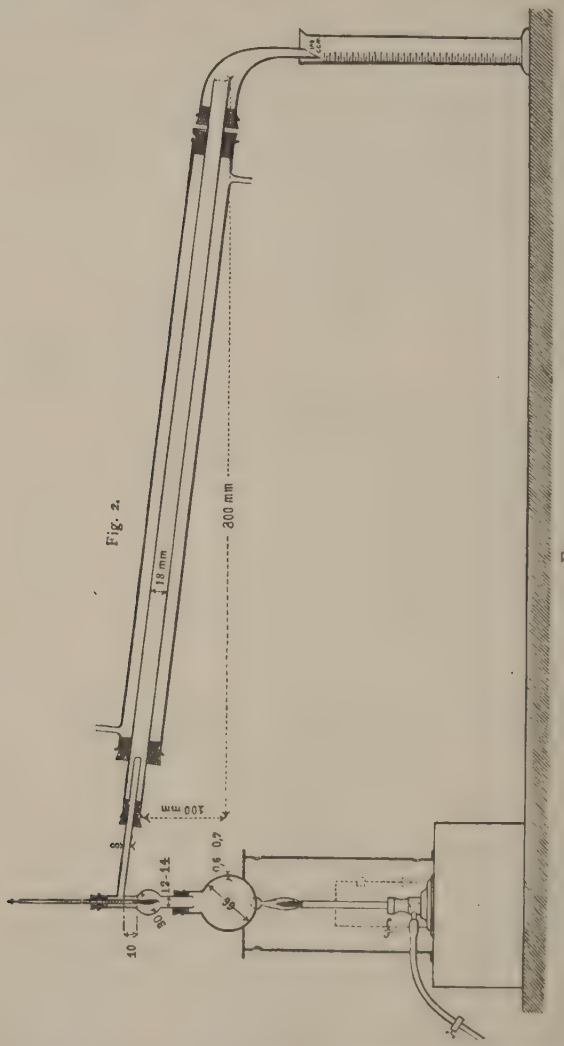
4. The Liebig cooler, *f*, is 800 mm. long, 18 mm. wide, and has such an inclination that the outlet of the inner tube is 100 mm. below the inlet.

5. The charge is 100 c.c. The distillation has to be carried on in such manner that 5 c.c. pass over per minute—that is, about 2 drops per second. It is carried on until the measuring cylinder, *g*, is filled up to 95 c.c.

6. The thermometer should be made of thin glass. Its outside diameter should not be more than half the width of tube *b*. Its bulb should be placed in the centre of the bulb of *b*. For 90-per-cent. and 50-per-cent. benzol a thermometer is employed with divisions for each $\frac{1}{2}$° C.; for pure benzene and toluene, it should be divided into 0°·1 C.

The thermometer is preferably provided with a scale,

movable by means of a screw, which is set at 100 before every



test by distilling 100 c.c. of distilled water at the moment when 50 c.c. have distilled over. Such a thermometer shows 80 as

the boiling-point of pure benzene and 110° as that of pure toluene, whichever the barometric pressure may be, unless this has changed during these operations. Or else an ordinary thermometer is employed whose scale has been accurately compared with that of a standard thermometer, tested by the Reichsanstalt. In the latter case the boiling-point must be corrected for barometric pressure according to the rules given by Lenders (*Chem. Ind.*, 1889, p. 169) as follows: (*a*) To the percentage of distillate, obtained at 100° C. at barometric pressures between 720 and 780 mm., in order to reduce this to 760 mm., add or deduct for each millimetre in the case of 50-per-cent. benzol, 0·077; in the case of 90-per-cent benzol, 0·033. (*b*) When distilling between 720 and 780 mm., add or deduct to 100° C. for each millimetre in the case of 50-per-cent. benzol, 0°·0461 C.; in the case of 90-per-cent. benzol, 0°·0453 C.; in order to obtain the real temperature corresponding to 760 mm. (*c*) For *pure* hydrocarbons the difference of temperature for each millimetre between 720 to 780 mm. is in the case of benzene, 0°·043; toluene, 0°·047; xylene, 0°·052 C.

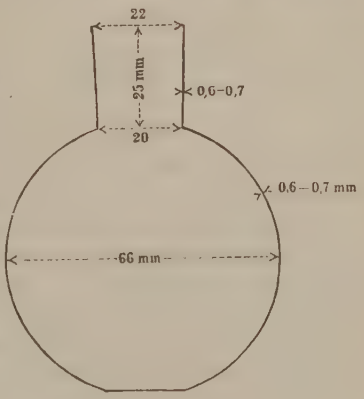


FIG. 198.

An example will make this clearer. Suppose we have distilled a 90-per-cent. benzol at a barometric pressure of 721·2 mm. (reduced to 0°) and obtained 88·8 per cent. distillate at 100°. $760 - 721{\cdot}2 = 38{\cdot}8$; $38{\cdot}8 \times 0{\cdot}033 = 1{\cdot}28$. Deducting this from 88·8, we obtain 87·5 as the real percentage of benzol.

When working according to these accurate and detailed descriptions, different chemists ought always to obtain the same results with the same material. If tested according to these prescriptions, commercial 90-per-cent. benzol should yield *at least* 90 per cent. at 760 mm. pressure when distilled up to 100 C. Usually 90 to 93 per cent. distil over. Commercial

50-per-cent. benzol should up to 100 yield at least 50 and up to 120 90 per cent., but 53 and 93 per cent. are tolerated.

The designation "per cent." in all these cases does not mean that "90-per-cent. benzol" contains 90 per cent. real benzene, C_6H_6, or "50-per-cent. benzol" 50 per cent. C_6H_6, the remainder being toluene, xylene, etc. Very different mixtures fulfil the ordinary testing conditions. The real average composition of commercial benzols has been found by Kraemer and Spilker, as the result of very numerous tests, to be as follows:[1]—

	Benzene.	Toluene.	Xylenes.	Cumenes.	Neutral naphthalene oils.
Benzol No. I. (so-called 90 per cent.)	84	13	3	...	...
" II. (so-called 50 per cent.)	43	46	11	...	...
" III. " "	15	75	10	...	...
" IV. " "	...	25	70	5	...
" V. " "	...	5	70	25	...
" VI. " "	...	...	35	60	5
Commercial "heavy benzol"	...	...	5	80	15

The last column ("neutral naphthalene oils") signifies the liquid companions of solid naphthalene, comprising much naphthalene, tetra-, penta-, and hexymethylated benzenes and other hitherto hardly known compounds. The above table does not take account of impurities, but only of the benzol hydrocarbons. The following table gives the average results of the products, obtained during six months at a large tar-works:—

	90-per-cent. commercial benzol.	50-per-cent. commercial benzol.	Commercial benzol, No. III.
	Per cent.	Per cent.	Per cent.
Water	0·060	...	...
Paraffins	0·100	0·25	0·50
Carbon bisulphide	0·086	0·39	...
Substances adding bromine, inclusive of thiophenes	1·202	1·23	0·82
Benzene	80·922	45·37	13·54
Toluene	14·850	40·32	73·42
Xylenes	2·180	12·14	11·69

[1] The designations "Benzol No. I," etc., are those mentioned on p. 742 as those usual in Germany.

The requirements concerning the behaviour in distillation of the various descriptions of commercial benzol[1] may be stated as follows, the figures denoting the *mininum* required :—

Commercial	90-per-cent. benzol	.	90	p.c.	up to	100°	C.	
„	50 „ „	.	50	„		100°,	90 p.c. up to	120°
„	benzol, No. III.	.	0	„		100°,	90 „	120°
„	„ IV.	.	0	„		120°,	90 „	145°
„	„ V.	.	0	„		130°,	90 „	160°
„	„ VI.	.	0	„		145°,	90 „	175°
„	heavy benzol	.	0	„		160°,	90 „	190°
Pure benzol should yield			95	per cent.	within	0°·8		
„	toluol „		95	„	„	0°·8		
„	xylol „		0	up to 136°,	90	per cent.	up to	140°
Cumole	„		0	„ 163°,	90	„	„	172°
Pseudocumol	„		0	„ 167°,	90	„	„	170°

Benzol free from thiophen has the same boiling-points as pure benzol.

In order to avoid the influence of *carbon bisulphide* on the testing of benzol, which frequently leads to awkward irregularities (*cf.* the statements of Watson Smith, p. 735), Nickels[2] treats the benzol twice with 10 per cent. by volume of a hot saturated solution of caustic potash in absolute alcohol, agitates for two hours, filters from the precipitate of potassium xanthate (*cf.* about this, *infra*, *sub* No. 4), removes the alcohol from the filtrate by twice washing with its own volume of water, removes the water suspended and dissolved by agitating with a little plaster of Paris, and distils as usual. Thus much more constant results are obtained than without that purification; the benzol now shows a lower sp. gr. (0·882 or 0·880, instead of 0·885), and is quite free from alliaceous smell.

If the object of testing benzol is not to conform to an arbitrary *commercial* standard, but to ascertain its *real composition*, the common retort or fractionating-bulb ought to be replaced by a more perfect apparatus for fractional distillation, *e.g.*, Linnemann's three-bulb tube, fitted with platinum-gauze cups, or a Le Bel-Henninger three-bulb tube, which is the apparatus most usually employed in England. A Hempel tube, as shown in Fig. 199, is quite as efficient and less liable to breakage; it is a simple tube, narrower at the bottom

[1] *Cf.* also p. 743.

[2] *Chem. News*, xliii., pp. 148, 250.

and with a side-branch near the top, filled with rough glass beads.

FIG. 199.

The following results were obtained by Mr B. Nickels from the same benzol (A, when distilled in an 8-oz. retort in the ordinary way; B, after removing the carbon bisulphide in the manner described above; C, when the *purified* benzol was

distilled in a three-bulb apparatus instead of in an 8-oz. retort):—

	A. Commercial 90-per-cent. benzol in 8-oz. retort.	B. A after being purified from CS_2 in 8-oz. retort.	C. B distilled in flask with three-bulb apparatus.
Spec. grav. at 15°·5 .	0·884	0·881	0·881
First drop distilled at .	79°·5	83°·4	...
5 per cent. " .	...	84°·2	81°·25
10 " " .	...	84°·3	82°·0
20 " " .	...	85°·0	82°·8
25 " " .	84°·0	...	...
30 " " .	85°·0	85°·8	83°·0
40 " " .	85°·4	86°·4	83°·5
50 " " .	86°·4	87°·1	84°·7
60 " " .	88°·0	88°·3	85°·3
70 " " .	90°·0	90°·0	86°·5
80 " " .	93°·0	93°·0	89°·3
90 " " .	100°·0	100°·0	100°·0
95 " " .	...	112°·4	111°·8

By operating on 300 c.c. of the same sample, removing the carbon bisulphide by alcoholic potash, and several times repeating the process of fractionating with the three-bulb apparatus, Mr Nickels obtained the following results as indicative of the proximate analysis of the benzol tested:—

	Per cent.
Carbon bisulphide	1·5
Light hydrocarbons, sp. gr. 0·872 (not nitrifiable, probably chiefly amylene and acetonitrile) . .	3·5
Benzene, sp. gr. 0·885, distilling within a range of 2° .	78·4
Toluene, sp. gr. 0·8715, distilling within 2° . .	16·6
	100·0

It is very desirable that the present empirical and conventional mode of benzol-testing should be replaced, at any rate in important cases, by the above scientific treatment.

2. *Specific Gravity.*

The specific gravity is usually only ascertained by the hydrometer, but for accurate purposes a Mohr's balance should be used. The average specific gravities of commercial benzols are stated by F. Frank (*Chem. Ind.*, 1901, p. 262).

Pure benzene	from 0·883 to 0·885
Benzene free from thiophen	„ 0·883 „ 0·884
Toluene	„ 0·870 „ 0·871
Xylene	„ 0·867 „ 0·869
Benzol, 90-per-cent.	„ 0·880 „ 0·883
„ 50- „	„ 0·875 „ 0·873
„ 0- „	„ 0·870 „ 0·872
Solvent naphtha boiling up to 160°	„ 0·874 „ 0·880
„ „ 175°	„ 0·890 „ 0·910
"Heavy benzol"	„ 0·920 „ 0·945

A lower specific gravity than the limit here given points to the presence of paraffins in more than usual quantity, a higher one in the case of Nos. I. and II., especially to carbon bisulphide, in Nos. III. to VI. to insufficient washing.

Haissig's attempt (*Chem. Zeit.*, 1897, p. 939) to draw conclusions on the composition of benzols from their specific gravities is proved to be untenable by a look at the above-given table, and has been expressly repudiated by Spilker and Bindewald (*ibid.*, 1898, p. 27).

3. *Test for Paraffins (admixture of Shale Oil, etc.).*

We first quote the test for paraffin, given by F. Frank and by Kraemer and Spilker as the most reliable:—Shake 200 g. of the sample in a separating-funnel with 500 g. of fuming sulphuric acid, containing 20 per cent. SO_3, during a quarter of an hour, avoiding a rise of temperature, and allow two hours for settling. Run off the acid and repeat the treatment with a fresh quantity of acid twice over, settling and drawing off the acid as before. When 1500 g. of that acid have been used, all the hydrocarbons, except the paraffins, are usually dissolved. Collect the oil by itself, and let the acid run in a slow stream on to its own weight of crushed ice, placed in a litre flask, with frequent shaking, so that the temperature does not rise over 40 .

Then distil over a free flame directly into a separating-funnel, holding 100 c.c. When, apart from the oil, 50 c.c. has passed over, you may count upon having recovered all the mechanically dissolved paraffin. Draw off the water, unite the paraffin with the oil previously collected, and shake repeatedly, each time with 30 g. of the fuming sulphuric acid, until no further diminution of volume takes place. Wash with a small quantity of distilled water and weigh the oil, which represents the paraffins contained in 200 g. of the benzol.

The word "paraffin" in this description denotes all substances which cannot be sulphonated or destroyed by fuming sulphuric acid. That means that any naphthenes present, as well as carbon bisulphide, are included among the paraffins. Since practically the designation "paraffin" is identified with "non-nitrifiable," the figures obtained as above are applicable to this (a direct estimation of the nitrifiable constituents will be described *infra*). If the carbon bisulphide has to be distinctly deducted, it must be estimated by one of the processes described *infra* in No. 4.

Benzols Nos. I. to III., as well as toluol, generally yield only a few tenths, up to at most 1 per cent. of paraffin. If more than this is found, it points to an adulteration with shale oil, petroleum, or the like.

To distinguish coal-tar benzol or naphtha from petroleum or shale-spirit, etc., which are also frequently called "benzoline, naphtha," etc., and which may easily occur as adulterations of the former, is not difficult. Both products can be at once distinguished by their smell, if unmixed; but in mixtures the smell of coal-naphtha prevails over even a very large addition of petroleum or shale-spirit. The specific gravity affords a good test (p. 762): with coal-naphtha it is always above 0·870 at 15°, with petroleum spirit, etc., below or at most very little above 0·700. There is, however, the drawback that carbon bisulphide *raises* the density of benzol, so that it would compensate a lowering produced by petroleum hydrocarbons. A direct estimation of the paraffin, as described above, gives an indication for the presence of shale oil, petroleum, and the like. Very distinct is the reaction with nitric acid, which at once acts upon the aromatic hydrocarbons of coal-tar, but hardly at all upon the fatty compounds of petroleum or paraffin oil.

The following useful synopsis of the characters of the two kinds of products has been made by A. Allen :[1]—

Petroleum spirit, Benzoline, Benzine.	*Coal-tar Naphtha, or "Benzol."*
1. Consists of heptane (C_7H_{16}) and its homologues.	1. Consists of benzene (C_6H_6) and its homologues.
2. Heptane contains 84·0 per cent. of carbon.	2. Benzene contains 92·3 per cent. of carbon.
3. Commences to boil at 54° to 60° C.	3. Commences to boil at about 80° C.
4. Specific gravity at 15·5 about 0·69 to 0·72.	4. Specific gravity about 0·880.
5. Smells of petroleum.	5. Smells of coal-tar.
6. Dissolves iodine, forming a solution of a raspberry-red colour.	6. Dissolves iodine, forming a purple-red liquid of the tint of an aqueous solution of potassium permanganate.
7. Does not sensibly dissolve coal-tar pitch, and is scarcely coloured by it even on prolonged contact.	7. Readily dissolves coal-tar pitch, forming a deep-brown solution.
8. When shaken cold with one-third of its volume of fused crystals of absolute carbolic acid, the latter remains undissolved and forms a separate lower stratum.	8. Miscible with absolute carbolic acid in all proportions.
9. Requires two volumes of absolute alcohol, or 4 or 5 volumes of methylated spirit of sp. gr. 0·828, for complete solution at the ordinary temperature.	9. Miscible with absolute alcohol in all proportions. Forms a homogeneous liquid with an equal measure of methylated spirit of sp. gr. 0·828.
10. Warmed with four measures of nitric acid of sp. gr. 1·45, the acid is coloured brown, but the spirit is little acted on and forms an upper layer.	10. Completely miscible with four measures of nitric acid of sp. gr. 1·45, with great rise of temperature and production of dark-brown colour. A portion of the nitrobenzene produced may separate out as the liquid cools.

No. 10 is capable of giving quantitative results in separating the two kinds of oil. The oil to be tested is treated with nitric acid of sp. gr. 1·45 in a small flask with an inverted condenser. When action has nearly ceased, the whole is poured into a narrow graduated tube; the measure of the upper layer indicates approximately the amount of petroleum spirit present. If the proportion of benzene is considerable, the nitrobenzene formed may not remain completely dissolved in the acid, but form a layer of dark-brown colour below the stratum of petroleum spirit. Nitrobenzene and petroleum spirit are readily miscible in the absence of nitric acid; but agitation

[1] *Chem. News*, xl., p. 101.

with strong nitric acid dissolves out the nitrobenzene, a portion of which may rise and form an intermediate layer, as above described.

Gawalowski[1] recommends as a reagent picric acid, which is easily soluble in coal-tar benzol but almost insoluble in petroleum spirit. If the latter is added to an equal volume of a concentrated solution of picric acid in benzol, the acid is precipitated in the form of crystals.

Holde[2] employs tar-pitch previously exhausted with boiling petroleum spirit. A gram or so of this pitch is placed on a small filter, and 5 c.c. of the liquid poured over it. From 5 to 10 per cent. tar-benzol in combination with petroleum spirit is recognized by the yellow colour of the solution, and an approximate colorimetric estimation can be thus performed.

For recognizing and estimating coal-tar benzol, etc., in the presence of rosin oil and mineral oils, Valenta (*Chem. Zeit.*, 1906, 266) shakes the mixture in a graduated cylinder with a solution of dimethyl-sulphate, which dissolves the benzol hydrocarbons easily, the rosin oil in the cold only with difficulty, and the mineral oils not at all.

The *nitrating test*, to be described now, was formerly very generally employed to find the real benzol, as distinct from the "paraffin." It is weighted by some errors, but we shall describe it here, since it is still a good deal in use, as giving an idea of how much nitrobenzene may be expected on the large scale:—Place 100 c.c. benzene in a flask of about 500 c.c. capacity, provided with a dropping-funnel, *a*, and a long tube, *b* (Fig. 200), for condensing any hydrocarbon volatilizing. Prepare a mixture of 150 g. nitric acid of sp. gr. 1·4, and 180 or 200 g. sulphuric acid, sp. gr. 1·84, which must be allowed to cool before use. Run this, drop by drop, through the tap-funnel *a* into the benzol, shaking this up almost constantly. As soon as the temperature rises, cool the flask by immersing it in a dish full of water. When all the acid has been added, and when no further rise of temperature takes place spontaneously, heat the flask gently for an hour or two (during this time the tube *b* is best replaced by a proper reflux-condenser). Allow the whole to settle, and separate the lower acid layer by means of a separating-funnel from the crude nitrobenzene. Dilute the acid

[1] *Chem. Centr.*, 1897, i., p. 1038. [2] *Fischer's Jahresber.*, 1895, p. 554.

with several times its bulk of water; any oily liquid separating after a few hours' rest is added to the nitrobenzene. Wash the crude nitrobenzene three times with its own bulk of water, once with a very dilute solution of caustic soda (if this solution is employed too concentrated, an emulsion is formed which is very awkward to manage), and again with water, taking care that no oil is lost in separating the washings. The well-settled liquor can be at once tested for its specific gravity, which, in the case of 90-per-cent. benzol, ought to be 1·20; with 50-per-cent. benzol, 1·19 at 15°; but this is not decisive, as the nitrobenzol is not quite free from water, and some benzol may have escaped nitrification. The liquor is therefore distilled from a fractionating-flask (Fig. 199, p. 760) till the temperature has reached 150°, and the distillate is once more nitrated, but this time with large excess of the acid mixture; anything remaining undissolved may be regarded as non-nitrifiable hydrocarbons. Theoretically, 100 parts of benzene furnish 157·6 of nitrobenzene; 100 parts of toluene, 148·9 of nitrotoluene.

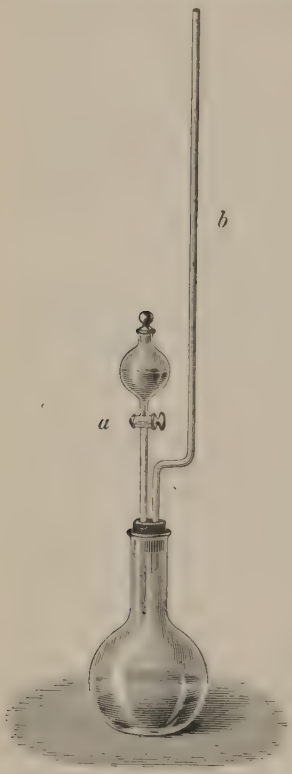


FIG. 200.

4. *Titration with Bromine.*

The object of this is to ascertain how far the purifying operations have removed the substances which add bromine and are resinified in practical use. This test is, therefore, applied only to *washed* benzol and toluol; it is not applicable to xylol and those commercial benzols which contain a considerable quantity of it, since the higher homologues of benzene even in the pure state are not any more indifferent to bromine.

Häussermann (*Chem. Zeit.*, 1887, p. 303) certainly contends that ordinary purified benzol, Nos. I. and II., gives no reaction with bromine, although it may contain useless hydrocarbons (paraffins), but the object of the test is to indicate just those hydrocarbons which add bromine.

The following prescriptions for this test are given by F. Frank and by Kraemer and Spilker. The test liquor is a decinormal solution of potassium bromide-bromate, prepared by dissolving 9·9167 g. KB+2·7833 $KBrO_3$ in a litre of water, and giving out 0·008 g. bromine per cubic centimetre on the addition of dilute sulphuric acid. Put 5 c.c. of the sample into a stoppered jar holding about 50 c.c., add 10 c.c. of dilute (20 per cent.) sulphuric acid, and quickly add as much of the bromine test liquor as the sample takes up after shaking it up uninterruptedly for five minutes. The end of the reaction is indicated when the oil, floating on the top, after fifteen minutes' standing, shows an orange-red colour, and when a drop of it, put on freshly prepared zinc-iodide starch paper, *momentarily* produces a dark blue colour. The number of cubic centimetres of the bromine solution used is stated as such. It is best to make a preliminary test before the proper one. "Pure" benzene and toluene should give a distinct reaction after adding 0·1 c.c. of the bromine solution; commercial 50-per-cent. and 90-per-cent. benzols on the average require 0·6, rarely over 1 per cent., but commercial xylol discolours after two minutes about 2 per cent. bromine, and much more after standing for some time.

5. *Testing with concentrated Sulphuric Acid.*

On being mixed with a large quantity of strong sulphuric acid, say 20 : 1, *pure* benzene and toluene are hardly coloured at all, other benzols take a yellow colour which should be as slight as possible. The observations of different analysts as to this colour cannot be directly compared by general expressions, wherefore F. Frank and Kraemer and Spilker give the following exact prescriptions for testing 90-per-cent. and 50-per-cent. benzol, pure benzene, toluene, and xylene.

Shake 5 c.c. concentrated sulphuric acid with 5 c.c. of the sample in a 15 c.c. stoppered bottle vigorously for five minutes, allow to stand one or two minutes, and then compare with a

solution of potassium bichromate in pure 50-per-cent. sulphuric acid, contained in a small stoppered bottle, exactly like the first, holding 5 c.c. of that solution + 5 c.c. purest benzene. When thus compared, 50-per-cent. and 90-per-cent. benzol should exhibit a colour like that of a solution of 0·5 to at most 1·5 g. chemically pure potassium bichromate in 1 litre of 50-per-cent. sulphuric acid. Xylol will have a colour like a solution of 1·2 to 2·0 bichromate per litre; with "pure" benzene and toluene the sulphuric acid should give no colour at all. The colour of the bichromate solution used as type keeps for a long time, but the pure benzene, used for the top layer, should be renewed every time.

The German Inland Revenue Office has adopted this method for testing the benzol No. I. (90-per-cent.), used for denaturing spirits of wine. The higher benzols, No. II. to VI., may also be examined in this manner, but they may yield very different results according to the use for which they are intended.

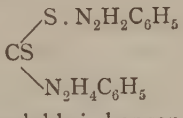
6. *Testing for the Smell.*

The smell of thoroughly washed benzols is mild and pleasantly aromatic, whereas unpurified or imperfectly washed benzol has a sharp, disagreeable, or even empyreumatic smell. It is observed by pouring a few drops on to pure filtering paper, and leaving it to evaporate in the air.

7. *Examination for Carbon Bisulphide.*

Liebermann and Seyewetz (*Ber.*, 1891, p. 788) have indicated the following reaction for discovering the presence of CS_2 in benzol, based on a previous observation of E. Fischer's. They agitate 10 c.c. of the benzol with 4 or 5 drops of phenylhydrazine several times during 1 to 1½ hours. If 0·2 per cent. CS_2 be present, a thick, white, crystallized precipitate is formed, converting the whole liquid into a magma. In the presence of 0·03 per cent. CS_2 the precipitate is still quite plainly visible; at 0·02 per cent. (0·17 g. per litre), the limit of the reaction is reached, and it is best to promote the crystallization by throwing in a tiny crystal of the compound

formed. This is the phenylhydrazine-phenylsulfocarbazinate, discovered by E. Fischer:



Fusing-point 97° C., insoluble in benzene, easily soluble in acetone, precipitated from that solution in orange-coloured flakes. It is very quickly decomposed on keeping, or by contact with water.

Liebermann and Seyewetz (*Berl. Ber.*, 1891, p. 788) mention that reaction as available also for a quantitative estimation of CS_2 in benzols. According to Frank (*Chem. Ind.*, 1901, p. 262), this method, although very accurate, has not found entrance in the works' laboratories, as being too lengthy and troublesome.

The presence of CS_2 can be also detected by alcoholic potash, which forms crystals of potassium xanthate (see below), or by alcoholic ammonia, which forms ammonium sulphocyanide, easily recognizable by the blood-red reaction with ferric chloride. J. B. Cohen[1] has tried to apply Traube's capillarometer (devised for estimating fusel oil in spirit-of-wine) for discovering carbon bisulphide, as fatty hydrocarbons, in benzol. His own paper shows that this reaction can hardly as yet lay claim to more than a qualitative value.

Quantitative estimation of Carbon Bisulphide in Benzol.

Holland and Phillips[2] put 2 c.c. of the benzol to be tested into a piece of combustion-tubing about 12 or 13 inches long, sealed at one end and drawn out at the other extremity, so as to form a funnel; they add 5 c.c. of a solution of ferric chloride, containing 240 g. Fe_2Cl_6 in 1000 c.c., and 10 c.c. of strong ammonia. The tube is carefully sealed before a lamp and well shaken; it is then wrapped in a cloth and immersed in boiling water for an hour or so. At the expiration of that time the tube is taken out, allowed to cool, and opened. The following reaction will have taken place in the first instance:—

$$CS_2 + 4NH_5O = NH_4 . CNS + (NH_4)_2S + 4H_2O,$$

but the presence of ferric chloride will have caused the sulphur

[1] *Chem. News*, 1886, p. 3016. [2] *J. Soc. Chem. Ind.*, 1884, p. 296.

of the ammonium sulphide to be converted into FeS. This is now oxidized along with the sulphur of the thiocyanate in the following manner:—The contents of the tube are transferred to a flask holding about ½ litre and are evaporated, just to dryness, by careful manipulation over a Bunsen flame: 20 c.c. of fuming nitric acid is added, and the whole is boiled nearly to dryness. If any sulphur is left unoxidized, a little more nitric acid must be added. Lastly, hydrochloric acid is added and some water, the solution is filtered, and the sulphuric acid in the filtrate is determined in the usual manner as barium sulphate. As it is not possible to get the whole of the ferrous sulphide out of the tube with water alone, this is best done by means of a little hydrochloric acid and a few grains of potassium chlorate.

Holland and Phillips have tested the accuracy of their method by a number of very satisfactory experiments with mixtures of known quantities of CS_2 and absolutely pure benzene, and have thereby obtained from commercial samples the following results:—

CS_2 contained in:—

Ordinary Lancashire tar-benzols:

50-per-cent. benzol . (*a*) 1·165; (*b*) 0·825; (*c*) 0·894 per cent.
90 „ „ . (*a*) 1·625; (*b*) 1·975; (*c*) 1·930 „
Touol . . . . (*a*) 0·164; (*b*) 0·170 per cent.

Carbonizing-benzols (various samples):

0·178; 0·131; 0·174; 2·450; 0·134; 0·246 per cent.

Ordinary crude naphthas:

0·143; 0·207 per cent.

Specially purified benzols:

50-per-cent. = 0·192; 90-per-cent. = 0·204.

"Pure benzene" from various dealers in chemicals:

0·716; 0·551; 0·722; 0·684 per cent.

They add that their method will return any other sulphur compounds present in benzol as carbon bisulphide, but that these bodies are only present in small quantities and are also impurities.

[Thiophen, according to a private communication from V. Meyer to the author, would *not* be acted upon by the above-

described treatment. *Cf.* also, later on, the statement of Irwin.]

The most usual method for estimating the CS_2 in benzol is based on transforming it into copper xanthate. We quote only the most recent communications on this subject.

Stavorinus (*Chem. Centr.*, 1906, i., 705) transforms the CS_2 into xanthogenate, oxidizes the sulphur by means of hydrogen peroxide, and estimates this gravimetrically or volumetrically.

The following is a prescription for carrying out the xanthogenate test, as generally used in Germany (Frank, *loc. cit.*; Kraemer and Spilker). Mix 50 g. benzol with 50 g. alcoholic potash solution (prepared by dissolving 11 g. caustic potash in 90 g. absolute alcohol), and let the mixture stand at ordinary temperature for some hours. Add about 100 c.c. water, shake well up, separate the aqueous liquor from the benzol and wash this several times with water. Unite all the aqueous liquids, and estimate the potassium xanthogenate formed from the CS_2 by the reaction:

$$CS_2 + KOH + C_2H_6O = H_2O + CS(O.C_2H_5)SK,$$

by titrating it with a copper solution containing per litre 12·475 g. crystallized copper sulphate, and indicating per cubic centimetre 0·0076 g. CS_2. For this purpose neutralize the solution with acetic acid, and add the copper solution until a drop, taken out with a glass rod and placed on a piece of filter-paper beside a drop of a solution of potassium ferrocyanide, produces a red colour at the point of contact. The final point is also approximately indicated by the fact that the precipitated cupric xanthogenate which is at first in the shape of fine powder, aggregates in the shape of lumps. The quantity of potash indicated above is sufficient up to a percentage of 5 per cent. CS_2 in the benzol. This will be enough in most cases, since even the richer benzols rarely contains upwards of 1 per cent. CS_2, and the poor ones none at all.

Edward C. Johnson (*J. Amer. Chem. Soc.*, xxviii., p. 1209; *Chem. Centr.*, 1906, ii., 1283) shows that the composition of the cuprous xanthogenate is not constant, and the sulphur is then found too low, on an average by 10 per cent. He assumes the proportion of CS_2 to the xanthogenate to be on the average =

1 : 1·750. The composition of the precipitate is influenced by its quantity and by the time it remains in contact with the mother-liquor. The total sulphur is found by evaporating the sample in a current of hydrogen and burning the vapours in an atmosphere of oxygen, whereupon the sulphur is estimated in the ordinary way.

Bay (*Comptes rend.*, cxlvi., p. 132) employs the reaction of Liebermann and Seyewetz (*supra*, p. 769), in the precipitation of CS_2 with phenylhydrazine, quantitatively. The compound formed is $CS_2(C_6H_5 . NH . NH_3)_2$, white, crystalline, very unstable in solution, and slightly so in the dry state, but it will keep long enough if a determination is effected in the course of a day. The precipitation is complete in 2 or 3 hours. Double, tared filters are used, the excess of phenylhydrazine is carefully washed out with pure benzene and the precipitate is dried in a vacuum. The results are a little high, owing to the difficulty of washing the precipitate completely.

8. *Testing for Thiophens.*

The reactions proving the presence of thiophen in benzol were partly known before its discovery, but erroneously ascribed to benzene itself.

Laubenheimer's indophenine reaction is carried out as follows:—In a small porcelain dish, previously rinsed with pure sulphuric acid, place a grain of isatine, into this a few cubic centimetres pure concentrated sulphuric acid, and into this the benzol to be tested. Put a watch-glass on and leave standing. If any thiophen be present, blue rings will appear in the benzol, the following reaction taking place:—

$$\underset{\text{Isatin.}}{C_8H_5NO_2} + \underset{\text{Thiophen.}}{C_4H_4S} = \underset{\text{Indophenin.}}{C_{12}H_7NOS} + H_2O$$

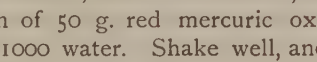
Thus as little as 0·01 per cent. thiophen may be discovered. *Cf.* V. Meyer (*Ber.*, 1882, p. 2893), Bauer (*ibid.*, 1904, p. 1244), Storch (*ibid.*, 1904, p. 1961).

Liebermann's reaction consists in shaking the benzol with a few drops of "nitrous vitriol" (concentrated sulphuric acid, containing a little nitroso-sulphuric acid). This produces first a green, then a blue colour, by the formation of the compound $C_8H_5NS_2O_2$. This reaction fails when very

little thiophen is present (especially in benzols manufactured during recent years, as shown by Schwalbe, *Ber.*, 1904, p. 324), but Liebermann and Peus (*Ber.*, 1904, p. 2461) have improved it even for this case, by pouring off the benzol and adding to the acid at the bottom a great excess of sulphuric acid. Thus 0·1 per cent. thiophen can be found.

Denigès[1] estimates the thiophens as follows:—In a stoppered 60 c.c. bottle 20 c.c. mercurial solution (prepared by dissolving 50 g. HgO in 200 c.c. concentrated sulphuric acid and diluting to a litre) is shaken with 2 c.c. benzol and heated, with agitation, on a boiling water-bath for an hour. After cooling, the precipitate is collected on a weighed filter, washed with hot water, and dried at 110° or 115°. Its weight multiplied by 0·0758 represents the thiophen.

The process of Denigès can be carried out volumetrically as follows (*Bull. Soc. Chim.* [3], xv., p. 1064):—Mix 2 c.c. benzol with 30 c.c. methyl alcohol, free from acetone, and quickly add 10 c.c. of a solution of 50 g. red mercuric oxide in 200 c.c. sulphuric acid and 1000 water. Shake well, and after twenty-four hours filter off the compound formed.



Put 21 c.c. of the filtrate, corresponding to 1 c.c. benzol, in a litre flask, and add 350 c.c. water, 15 c.c. liquor ammonia, 10 c.c. of a solution of potassium cyanide equivalent to a decinormal solution of argentic nitrate, and 5 or 6 drops of a 20-per-cent. solution of potassium iodide. Clear up the solution in case of need by heating, and add $1/n$ argentic nitrate solution up to the formation of a permanent cloud. If n be the number of c.c. of the silver solution used, the quantity of thiophen contained in 1 litre of the benzol is $=(n-0{\cdot}3 \text{ c.c.}) \times 2{\cdot}8$ g.

Dimroth (*Ber.*, 1902, 2035) found that at 100° C. thiophen is acted upon by a solution of mercurous acetate, while benzol remains unchanged. He proposes this reaction as a basis for the estimation of thiophen in benzol.

Kreis (*Chem. Zeit.*, 1902, 523) proves the presence of thiophen in benzol by the (soon evanescing) coloration produced by thallin.

[1] *Comptes rend.*, cxx., p. 781.

This reaction may be also applied for testing for thiotoluene in toluene, but it fails with thioxenes.

Schwalbe (*Chem. Centr.*, 1905, ii., pp. 335 and 1126) declares the methods of Denigès and Dimroth not to be accurate. He employs the indephenin reaction (*vide supra*) to quantitative colorimetric estimations, by which he can estimate 0·05 per cent. thiophen in a shaking-cylinder, and down to 0·01 in an open dish.

9. *Testing for Total Sulphur.*

Irwin (*J. Soc. Chem. Ind.*, 1901, pp. 440) justly contests the assertion made by Holland and Phillips (p. 769), according to which their method renders the total sulphur contained in benzol, whereas it acts only on carbon bisulphide. He therefore proceeds as follows (Fig. 201). Into a spirit lamp, A, holding 100 c.c. he puts 10 c.c. of the benzol with 90 c.c. pure alcohol or methylated spirits (the latter to be tested for sulphur in the same apparatus), shakes up, and lights the lamp. Round the wick he puts some pieces of carbonate of ammonia, F, and covers it with the bent funnel, B, just as is done in the ordinary testing of coal-gas for sulphur. The flame must not be too large, otherwise it will smoke, and no more wick than is absolutely necessary must be used. The gases pass through the apparatus C, filled with moist glass beads, where the sulphur is retained; C is at the end washed out into E, and the sulphuric acid formed is estimated as $BaSO_4$. If we call the weight of the latter n, then the term $\frac{n \times 32 \times 1000}{233 \times 10}$ expresses the number of grams of S per litre. The results are rather too low, but sufficient for practical purposes.

Johnson (*J. Amer. Chem. Soc.*, xxviii., p. 1209) describes an apparatus for burning the benzol vapour in an oxygen atmosphere, absorbing the gases formed in a suitable way and estimating therein the S in the usual way.

10. *Quantitative Estimation of the Pure Benzenoid Hydrocarbons in Commercial Benzols.*

This is sometimes necessary for the purpose of the colour-manufacturer or other synthetic operations. In Germany, according to the description of Frank (*Chem. Ind.*, 1901, p. 265), a kilogram of benzol is distilled from a copper-retort (as shown

in Fig. 202), on which a Le Bel-Henninger column (p. 781) 2 ft. long is placed. The thermometer must have an adjustable scale, or else its indications must be corrected by the rules given by Lenders (p. 757). The position of the coolers, its width, and the rate of distillation are adjusted as described on p. 781.

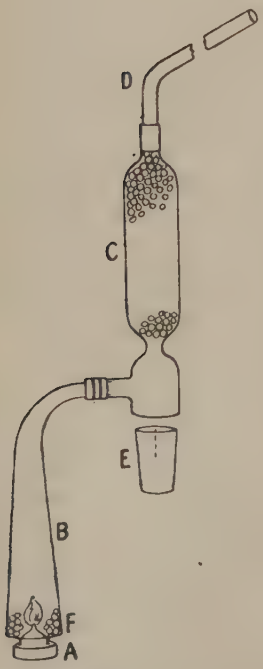


FIG. 201.

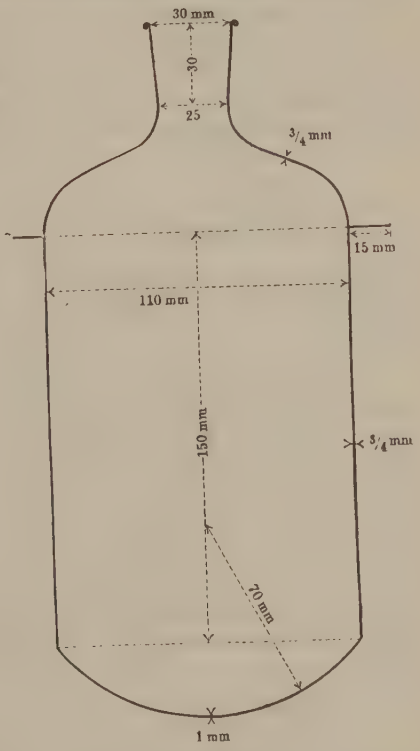


FIG. 202.

The distillates are collected in tared glass bottles. The single fractions are taken as follows:—

(1) With 90- and 50-per-cent. benzol:—

First runnings . . .	up to 79° C.
Pure benzene	from 79° to 85°.
Intermediate fraction . .	„ 85° „ 105°.
Pure toluene	„ 105° „ 115°.
Xylene	over 115°.

(2) With "pure benzol":—

First runnings	up to 79°.
Real benzene	from 79° to 81°.
Last runnings	over 81°.

(3) With "pure toluol":—

First runnings	up to 79°.
Real toluene	from 109° to 110°·5.
Last runnings	over 110°·5.

(4) With xylol:—

First runnings	up to 135°.
p-Xylene	from 135° to 137°.
m-Xylene	„ 137° „ 140°.
o-Xylene	„ 140° „ 145°.
Last runnings	over 145°.

When tested according to these prescriptions, commercial benzols, according to Frank, yield on the average the following results:—

	90-per-cent. benzol.	50-per-cent. benzol.
First runnings	1·0	0·3 per cent.
Benzene	78·8	18·3 „
Intermediate fraction	10·0	47·5 „
Toluene	8·0	23·7 „
Xylene	2·0	10·0 „
Loss	0·2	0·1 „

	Pure benzol.
First runnings	0·5 p.c.
Benzene	98·0 „
Last runnings	1·2 „
Loss	0·3 „

	Pure toluol.
First runnings	0·3 p.c.
Toluene	97·3 „
Last runnings	2·2 „
Loss	0·2 „

	Xylol.
First runnings	1·3 per cent.
Paraxylene	15·0 „
Metaxylene	76·5 „
Orthoxylene	5·0 „
Last runnings	2·0 „
Loss	0·2 „

The presence of *toluene* in "pure benzol," according to Raikow and Uerkewitch (*Chem. Zeit.*, 1906, 295), is recognized by nitrating the benzol and adding caustic soda, which at the ordinary temperature does not act upon nitrobenzene, but produces a brown colour with nitrotoluene.

Charitschkow (*Chem. Centr.*, 1907, i., 1738) separates the aromatic hydrocarbons by fractionated precipitation from the alcoholic solution.

A special method for the testing of commercial *xylol*, in order to determine the quantity of the *three isomeric xylenes and of neutral oils*, has been published by Levinstein,[1] based on the behaviour of those substances towards nitric acid, concentrated sulphuric acid, and fuming oil of vitriol. This is very important, since the commercial xylol, although boiling within two degrees, contains the three isomers in very different quantity, while only one of them, metaxylene, is of technical importance. The method is as follows:—

A. *Estimation of Metaxylene and Paraffins.*—Heat 100 c.c. of the crude xylol to 100° in a sand-bath, together with dilute nitric acid (40 c.c. acid of sp. gr. 1·40 and 60 c.c. of water), from half an hour to an hour, or until red fumes are no longer evolved, taking care to thoroughly mix the acid with the hydrocarbons; separate the latter from the acid, add to the hydrocarbons an excess of caustic soda, and distil by wet steam. The distillate consists of water and metaxylene, mixed with paraffins. The hydrocarbons are separated from the water, and about $1\frac{1}{2}$ of their volume of concentrated sulphuric acid is added and well mixed for half an hour, when the metaxylene will be dissolved, leaving the paraffins unaltered. Instead of distilling the above mixture, several times washing with caustic soda will be sufficient; the ortho- and paratoluene have been converted into toluic acids or their nitro-compounds, and are removed by the soda, whilst metaxylene is very little altered by the treatment with dilute nitric acid. The c.c. of metaxylene plus paraffin, and then the c.c. of the latter alone, are read off, and at once indicate percentages.

B. *Estimation of Paraxylene.*—Take 100 c.c. of the crude xylene, agitate with 120 c.c. concentrated sulphuric acid (170° Tw.) for half an hour, cooling the mixture till no more is dissolved, and allow to settle. The residual hydrocarbons, consisting of paraxylene and paraffins, are separated, measured, and heated for a short time on a water-bath with fuming sulphuric acid containing 20 per cent. SO_3; allow to settle, and separate the paraffin, which is again measured.

[1] *J. Soc. Chem. Ind.*, 1884, p. 77; *cf.* also *supra*, pp. 184 and 739.

C. *Estimation of Orthoxylene.*—In ordinary xylene from English gas-tar, orthoxylene may be estimated by difference, the two other xylenes and the paraffins having been estimated as above. But since toluene, cumene, and cymene are also acted upon by dilute nitric acid, samples containing these should be treated in the following way:—Employ part of method B to effect the separation of the paraffins and the paraxylene from the crude xylene; convert the meta- and orthosulphonic acids into their calcium salts and afterwards into their sodium salts; concentrate the solution of the latter, when the ortho-salt will crystallize in large prisms, while the meta-salt remains in solution; concentrate the solution still more, and recrystallize the first and second crop of crystals. The ortho-salt will then be obtained in large, well-developed crystals, which are easily distinguished from the indistinct crystals of the meta-salt, if such are mixed with it. Scotch xylenes furnish the ortho-salt much less easily than English, even when the latter contain much less orthoxylene, probably owing to the complications caused by the presence of non-saturated hydrocarbons. Method B and the additional method just described, are of little practical importance, since the buyer only requires to know the percentage of metaxylene; but method B is a good check upon method A.

Levinstein in this manner obtained the following result with different descriptions of commercial xylene:—

Origin.	Sp. grav. at 19°	Distils at °C.	Meta-xylene.	Para-xylene.	Ortho-xylene.	Paraffins.
Pure metaxylene obtained by method A . .	0·8668	142-143	100	0	0	0
English (from Manchester tar)	0·8629	134-140	87	6	4	3
English	...	140-143	87	4	6	3
,, ...	...	141-145	83	5	7	5
,, ...	0·8660	138-141	79	3	15	3
Scotch	0·8574	134-140	72	8	12	8
Unknown . . .	...	139-141	70	5	15	10
English and Scotch mixed	0·8605	134-141	81	10	3	6
,, ,,	...	136-142	86	6	4	4
,, ,,	0·8613	136-141	86	6	2	6
,, ,,	...	140-141	86	3	5	6
?	0·8600	136-142	85	6	3	6
Xylene from coal-gas .	...	138-144	47	8	13	26

Levinstein himself only claims approximate accuracy for his

method. A. Reuter[1] objects to it that very dilute nitric acid does not fully remove the isomers of metaxylene, and that an acid of the concentration prescribed by Levinstein acts only upon metaxylene and oxidizes it into metatoluic acid. Moreover, paraxylene is acted upon by ordinary sulphuric acid, although less so than its isomers. The presence of paraffins greatly increases the resistance of all the isomers. Lastly, the paraffin can only be freed from the last traces of xylenes by employing a great excess of fuming sulphuric acid.

The analyses given by Levinstein are also at variance with the statement by Noelting, Witt, and Forel (*Berl. Ber.*, 1885, p. 2068), that they always found at least 25 per cent. paraxylene in commercial xylol.

Radzizewski and Wispek[2] state that very small quantities of paraxylene can be detected in ortho- or metaxylene by treating the hydrocarbons with an insufficient quantity of bromine (*e.g.*, 24 parts bromine to 10 parts of the hydrocarbons); in that case the paraxylene bromide separates first on cooling, in the shape of a pulverulent precipitate cooling at 143°·5.

Compare also the methods of Reuter and of Crafts, described pp. 739 and 740, which are intended for separating the isomers in bulk.

A method for separating the two *trimethylbenzenes* (pseudocumene and mesitylene) has been described by Jacobsen. It is founded upon converting them into sulphamides, separating these by alcohol, and regenerating the hydrocarbons by fuming hydrochloric acid. Up to the present time no technical use has been found for this method.

Weger (*Z. angew. Chem.*, 1909, p. 341) does not consider Levinstein's method to be accurate (which is not claimed by its author himself; *vide supra*). He is not aware of any satisfactory analytical method for the separation of the three xylenes.

11. *Practical Tests in the Laboratory for Final Products on a Larger Scale.*

At one of the largest German aniline works the following process is employed for *testing commercial benzol*:—(1) *Preliminary test*—Twenty c.c. pure concentrated sulphuric acid is

[1] *Ber.*, 1884, p. 2028. [2] *Ibid.*, 1885, p. 1280.

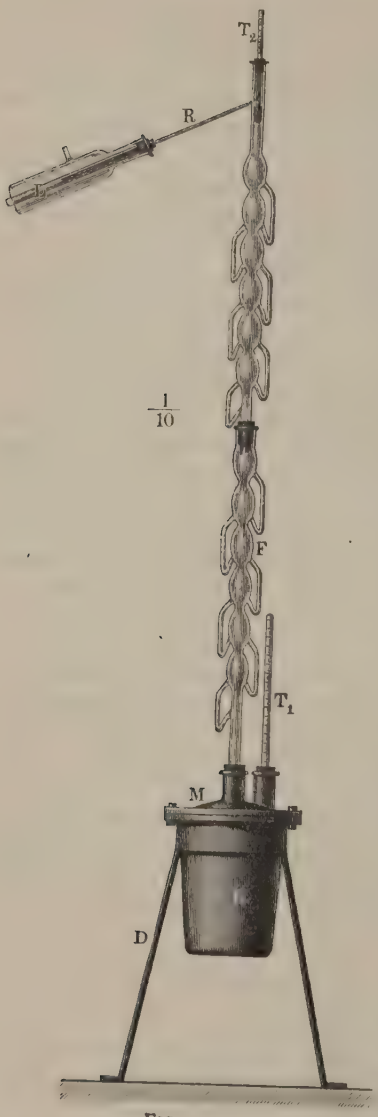


FIG. 203.

shaken with 1 c.c. benzol in a stoppered bottle, and allowed to stand for 12 hours. The colour ought not to be more than light yellow. (2) *Purification.* —One thousand grams benzol is shaken with 125 g. concentrated sulphuric acid for half an hour in a large drop-funnel. If in the preliminary test the colour was strongly yellow, more acid, up to 200 c.c., must be taken. After settling, the acid is drawn off, the benzol shaken up 3 or 4 times with 200 c.c. water each time, and again 3 or 4 times with 1-per-cent. caustic-soda solution. Now 10 c.c. of the benzol is shaken with successive portions of 0·5 c.c. saturated bromine-water, until the benzol retains its yellow colour at least 2 minutes. It is then poured back to the main portion. If more than 1·5 c.c. bromine-water has been used in this test, the sulphuric-acid washing should be repeated with another 50 c.c. of acid, and this again repeated until in the above test no more than 1 or 1·5 c.c. bromine-water is used. The washed benzol is now dried by occasionally shaking up

with fused calcium chloride for 2 hours, and the loss by the purifying process is ascertained by weighing it. (3) *Fractionating*—The purified benzol is put into the copper retort K, Fig. 203, placed on a tripod, D. The cover M is screwed on; it is provided with an opening for the thermometer T_1 and the Le Bel-Henninger fractionating-head F. The latter (in two pieces) consists of 12 bulbs, with platinum-wire gauze in each, and measures up to the side-tube R. In the top thermometer T_2 is fixed so that the bulb is just on a level with the lower part of the side-tube R, which is connected with a Liebig cooler, L, 1 metre long. The distillation is carried on by means of a Bunsen burner, in such a manner that two drops fall per second. The distillates are collected in tared receivers and weighed. The fractions are made as follows:—(*a*) for 90-*per-cent. benzol*: first runnings, up to 79°; benzene, 79° to 85°; intermediate fraction I., 85° to 105°; toluene, 105° to 113°. When 113° has been reached, the distillation is interrupted and the residue in the retort is weighed; (*b*) for 50- to 90-*per-cent. benzol* and 0- to 90-*per-cent. toluol*: first runnings, up to 79°; benzene, 79° to 85°; intermediate fraction I., 85° to 105°; toluene, 105° to 113°; intermediate fraction II., 113° to 133°. At 133° the distillation is interrupted, the residue is weighed and treated with steam, and weighed again as "residue." The loss found by adding up the residue and all the fractions, is "loss in distillation." In reporting the results, 85 per cent. of the first runnings is calculated as benzene, 60 per cent. of intermediate fraction I. as benzene, and 40 per cent. as toluene. For intermediate fraction II. no fixed proportion has been ascertained. (4) *Estimation of fatty hydrocarbons.*—One hundred g. benzol is nitrated (*cf.* p. 765) with 125 g. sulphuric acid (1·84) and 125 of nitric acid (1·5) at not more than 30° C. The crude nitrobenzol is separated from the acid, neutralized with caustic soda, and distilled with steam until a sample of the distillate sinks in water. The distilled oil is separated from water and placed in a narrow graduated cylinder (50 c.c.), where from 15 to 40 c.c. of the above acid mixture is gradually and carefully added, with occasional shaking, until the volume of the oil ceases to diminish. By this treatment any unchanged benzene and toluene are dissolved in the acids; the fatty hydrocarbons float on the top and their volume

is read off. This is calculated as amounting to 60 per cent. of the actually present fatty hydrocarbons. This test is only made if there is reason to expect a somewhat large proportion of fatty hydrocarbons from the results of the purifying test.

Claudon & Morin[1] describe a small-scale column-apparatus (Figs. 204-207) for fractionating spirit, benzol, etc., which is

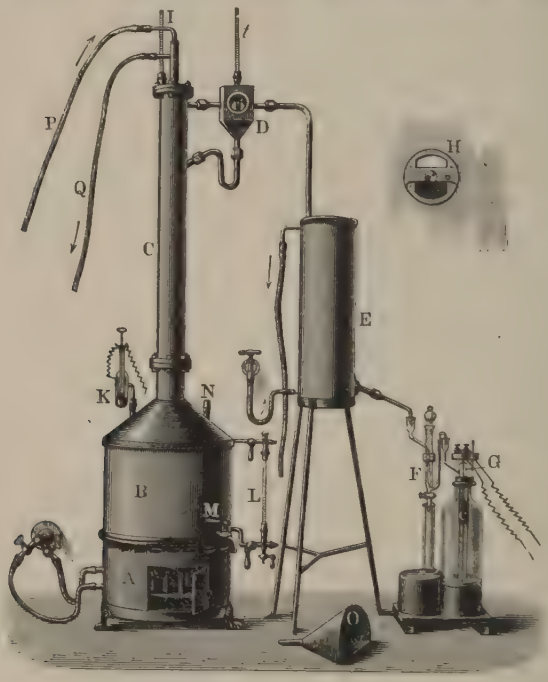


FIG. 204.

quite similar to the large-scale apparatus, and which I can recommend from practical experience. A (Fig. 204) is a double-ring gas-furnace. The bottom of boiler B is slightly inclined towards tap M, to facilitate emptying. N is a charging hole, with funnel, O, to fit in. Tube L is a liquor-gauge; K (of

[1] *Bull. Soc. Chim.*, xlviii., p. 804; *Z. angew. Chem.*, 1888, p. 85.

which the details are shown in Fig. 205) a pressure-gauge. Column C contains 10 plates, like the sieve-plates of large apparatus, easily cleaned and removed. The inner cooling-pipe I receives water from P, and the warm water runs off at Q. The "analyzer" D with thermometer *t*, catches any froth and returns it to the column. E is an ordinary cooler. The over-

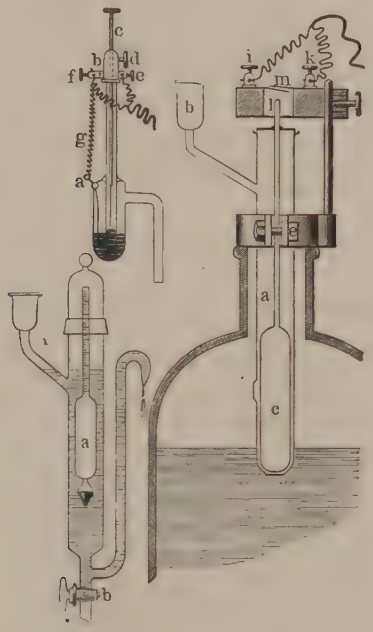


FIG. 205.

FIG. 207. FIG. 206.

flow vessel F (shown also in Fig. 207) admits of checking the specific gravity of the distillate by a hydrometer, *a*, and of taking samples at *b*. From here the distillate runs through funnel *b* and pipe *a* (Fig. 206) into bottle G. When this is full, float *c* rises and closes the contact *l m*, leading by *i k* to an electric bell. Rod *c* (Fig. 205) of the pressure-gauge K (Fig. 205) slides in a copper collar, *b*, and is fixed by screw *d*. When the pressure in the boiler rises above a certain height, the mercury in the gauge rises as well, and a platinum wire at the

bottom of *c* comes into contact with an electric bell, by means of *a*, *g*, *f*, and *e*. This is only required where several such apparatus are going at the same time. The distillation must be carried on slowly at the commencement, till all the plates are filled and the cooling-water is regulated.

A paper on the valuation of crude naphtha, etc., has been published by G. E. Davis.[1] He mentions that the method usually employed is to distil a quantity (generally 100 c.c.) in a tubulated glass retort, and to catch the quantity distilling over up to a temperature of 120° C., the bulb of the thermometer being immersed the whole time in the boiling liquid. The article is generally sold on the basis of an average yield of 30 per cent. at 120°, within a rising or falling allowance per degree, or every 1 per cent., within prearranged limits. This test has nothing to recommend it except its simplicity; and if buyers do not receive a sample, so as to judge for themselves, but only an account of the test, they may suffer great losses. Crude naphtha is valuable only for the benzene, toluene, and solvent naphtha it contains; but the distillation-test to 120° does not differentiate these products, nor does it take any account of the loss in washing with acid and alkali.—A much better test than the above is:—One hundred c.c. of the naphtha is distilled in a 200 c.c. flask, with a thermometer arranged so that the bulb shall be just off the bottom of the flask. The distillate is caught in a 100 c.c. graduated measure, and the yield at the following points taken: 100°, 110°, 120°, 140°, 170°, 200°. The quantity which shall have passed over at 140° is again distilled, and the yield at 100° and 120° noted. [This almost exactly agrees with the prescription given by the author so far back as 1867.] All that passes over up to 100° in the second distillation is called *benzol* (B); that which passes between 100° and 120°, in the second distillation is called *toluol* (T). *Best naphtha* (N_1) is that which passes between 120° in the second and 170° in the first distillation; *second naphtha* (N_2), that caught between 170° and 200° in the first distillation; and *creosote* (C), the balance. The following are some tests made by this method:—

[1] *J. Soc. Chem. Ind.*, 1885, p. 654.

Spec. grav.	First distillation.						Second.		Products.				
	100°	110°	120°	140°	170°	200°	100°	120°	B.	T.	N_1.	N_2.	C.
0·886	2	22	42	67	88	94	23	53	23	30	35	6	6
0·893	11	30	50	72	88	95	27	56	27	29	32	7	5
0·903	2	14	23	56	78	92	23	42	23	19	36	14	8
0·915	0	2	11	39	73	94	7	26	7	19	47	21	6
0·917	2	16	34	57	75	87	22	43	22	21	32	12	13
0·940	2	10	21	42	59	69	23	36	23	13	6	17	10

This method is, however, not yet accurate enough. The redistillation of a large quantity of the different fractions gave the following results :—

B . .	85°	90°	95°	100°	110°	120°
	2	48	71	80	90	95 per cent.
T . .	100°	110°	120°	130°	135°	
	47	75	86	94	96 per cent.	
N_1 . .	130°	140°	150°	160°	170°	180°
	13	43	63	79	91	93 per cent.
N_2 . .	160°	170°	180°	190°	200°	
	2	31	55	74	87 per cent.	

The "creosote" crystallized into a solid mass [probably naphthalene]. The above shows that the "benzol" is only of a strength of 80 per cent., the "toluol" is nearly a 50- to 90-per-cent. benzol, the naphthas N_1 and N_2 are mixtures of solvent naphtha and light oil. Neither does the just-described method take into account the products eliminated by washing with acid and soda. In a special case 1600 galls. of crude naphtha, tested by that method, yielded :—

25 B, 23 T, 32 N_1, 10 N_2, 10 C.

After washing there remained 1200 galls., which tested :—

26 B, 14 T, 24 N_1, 9 N_2, 27 C.

When this quantity was worked in a still of the best construction it yielded :—

348 gallons 90-per-cent. benzol = 23 per cent.
362 „ 50-per-cent. benzol = 24 „
156 „ solvent naphtha = 10 „

Hence the test would have led one to suppose that much more solvent naphtha [and less 50-per-cent. benzol] would be obtained than was actually the case.

Davis therefore recommends the following method [which practically agrees with the general prescriptions given by the author in the first edition of this work, pp. 251 and 252]:—

Two hundred c.c. of the crude naphtha are agitated with 20 c.c. concentrated sulphuric acid (rectified oil of vitriol) in a stoppered globular separating-funnel of 300 c.c. capacity. After agitating well for five minutes, allow to settle and run off the acid carefully, so that nothing is lost. (Sometimes two washings with 10 c.c. of acid each are preferable to one washing with 20 c.c.) Now wash twice with 30 c.c. of water, each time running off the wash-waters very carefully, then add 30 c.c. caustic-soda solution, of sp. gr. 1·060, and again wash with water. Pour the washed naphtha into a measuring-jar, and determine the percentage loss. All is now ready for the distillation. Measure off 100 c.c. of the washed naphtha, less the percentage loss, and place in a 200 c.c. flask fitted with a delicate thermometer and Glinsky's or Le Bel-Henninger's fractionating tubes (p. 781, or any other, preferably Hempel's glass-bead tube, which has been shown in Fig. 199, p. 760), connecting it with a Liebig's condenser of the ordinary pattern. Heat the flask with a rose-burner (Fig. 194, p. 748), and so regulate the flame that a drop distils over about once in every two seconds. Carry the distillation on until the thermometer has risen to 120°, catching the distillate in a graduated jar. At this point change the receiver, and catch all that comes over up to 170°. The distillate to 120° consists substantially of benzene and toluene; the portion distilling between 120° and 170° is solvent naphtha, the remainder creosote. The "solvent" produced in this small apparatus will show the first drop at 125° and 90 per cent. at 100°, which is usually the quality worked for on the large scale. The composition of the distillate to 120° will vary somewhat with every sample of crude naphtha operated upon. In Davis's own case the quantities yielded by each analysis were collected from many examples; and when mixed and tested in the usual way employed for 90-per-cent. and 50-per-cent. benzols, showed 64 per cent. at 100° and 93 per cent. at 120°. Davis states that

it is easy, by means of this method, without any supervision, to run the specified quantities of 90's and 50's from the still direct, without any fear of mistakes. The following table shows the results of the older methods compared with those of the new method :—

Spec. grav.	Old method.	Improved method (p. 784).					Davis's new method.				
	Per cent. at 120°	B.	T.	N_1.	N_2.	C.	Loss in washing.	Per cent. at 120°	Test at 1.0°	Per cent. solvent.	Creosote.
									Per cent.		
0·886	42	23	30	35	6	6	13·5	50	60	23	27
0·902	31	19	22	35	15	9	18·5	46	59	19	36
0·908	29	17	23	39	13	8	10·5	45	64	23	32
0·924	32	30	13	27	15	15	16·5	47	58	13	40

In order to rapidly estimate the quantities of 90-per-cent. and 50-per-cent. benzol and toluol which can be run from the still, Davis has constructed the following tables :—

A. Mixtures of 90-per-cent. benzol with 50- to 90-per-cent. benzol.

90-per-cent.	50- to 90-per-cent.	First drop.	Per cent. at 100°	Per cent. at 120°
0	100	92°	50	90
5	95	92°	51	92
10	90	91°	51·5	92
15	85	91°	53	92
20	80	90°	55	92
25	75	90°	60	93
30	70	90°	65	93
35	65	90°	67	94
40	60	88°	69	94
45	55	88°	70	94
50	50	87°	71	94
55	45	87°	73	94
60	40	86°	76	95
65	35	86°	78	95
70	30	86°	79	96
75	25	85°	84	96
80	20	85°	84	97
85	15	84°	86	97
90	10	84°	88	dry
95	5	84°	89	dry
100	0	84°	90	dry

B. Mixtures of 50- to 90-per-cent. benzol and commercial toluol.

50- to 90-p.-c. benzol.	Toluol.	First drop.	Per cent. at 100°	Per cent. at 105°	Per cent. at 110°	Per cent. at 200°
100	0	92°	50	68	80	91
95	5	93°	45	64	76	91
90	10	94°	33	60	73	90
85	15	94°	30	58	73	90
80	20	95°	28	57	72	90
75	25	95°	26	55	71	90
70	30	96°	22	48	67	90
65	35	96°	19	47	65	90
60	40	96°	15	46	65	90
55	45	97°	12	44	65	90
50	50	98°	8	42	64	90
45	55	98°	4	34	57	90
40	60	99°	0	26	56	90
35	65	100°	0	25	55	90
30	70	100°	0	23	53	90
25	75	100°	0	21	53	90
20	80	100°	0	16	48	90
15	85	101°	0	14	46	90
10	90	102°	0	13	45	90
5	95	103°	0	10	44	90
0	100	103°	0	0	39	90

C. Mixtures of 90-per-cent. benzol with commercial toluol.

90-per-cent. benzol.	Toluol.	First drop.	Per cent. at 100°	Per cent. at 105	Per cent. at 110°	Per cent. at 120
0	100	103°	0	7	50	94
5	95	102°	0	21	59	94
10	90	101°	0	30	66	94
15	85	100°	0	38	68	95
20	80	97°	9	43	73	95
25	75	95°	16	53	76	95
30	70	95°	23	59	78	96
35	65	94°	43	60	80	96
40	60	93°	43	66	82	96
45	55	92°	46	71	85	97
50	50	91°	52	72	86	97
55	45	91°	58	76	86	97
60	40	91°	60	78	88	97
65	35	90°	65	81	89	97
70	30	89°	71	83	91	97
75	25	88°	75	85	91	98
80	20	87°	77	87	92	98
85	15	86°	83	89	93	98
90	10	85°	85	91	94	dry
95	5	84°	88	93	95	dry
100	0	84°	90	94	96	dry

The *pecuniary valuation of crude naphtha* can be easily made, if the proper test has been applied. Davis quotes the following example. A sample, tested by his new process, yielded :—

Loss by washing . . . . 18½ per cent.
Distillate to 120° . . . . 45 per cent.
Test of same $\frac{100^{c}}{71}$ $\frac{120^{c}}{94}$.

[*i.e.*, 50 per cent. of 90-per-cent. and 50 per cent. of 50-per-cent. benzol, according to table A.]

Distillate to 170° . . . . 10 per cent.
Test of same $\frac{126^{c}}{0}$ $\frac{160^{c}}{92}$.

The quantities actually obtained from the still were :—

90-per-cent. benzol 23 per cent. at 1s. 7d., f.o.b. Goole, casks free.
50-per-cent. benzol 24 per cent. at 1s. 4d.
Solvent . . 10·4 per cent. at 9d.
Test of solvent $\frac{130^{c}}{1}$ $\frac{160^{c}}{94}$.
Loss by washing, 20 per cent.

Deducting 2d. per gall. for barrels, 2d. for carriage, and 1d. for sundries (leakages, super tares, etc.), this leaves at the works :—

90-per-cent. benzol 23 galls. at 1s. 2d. = 322d.
50 „ „ 24 „ 11d. = 264d.
Solvent . . 10 „ 4d. = 40d.

$$\frac{626}{100} = 6\tfrac{1}{4}\text{d.}$$

per gall. of crude naphtha, out of which the rectifier will have to find (apart from the price of the crude naphtha) vitriol, soda or lime, wages, steam, repairs, depreciation, sundry charges, and his profit, if there be one.

Usually much less complicated methods than Davis's are employed for testing crude naphtha for its commercial value. The following *empirical rules* are taken from *my own practice*, and by means of them the results to be expected on the large scale can be very approximately inferred from laboratory distillations, which will take hardly a quarter of an hour. They were elaborated before fractionating-bulbs had come into use, but they still hold good.

1st. One hundred c.c. of the oil is distilled from a glass

retort or fractionating-flask, and the distillate collected, (*a*) up to 140°, (*b*) from 140° to 170°. On each occasion, just as the required temperature is attained, the lamp is withdrawn, and the oil contained in the condenser is allowed to drain off before the receiver is changed; this makes a difference of several per cent. Suppose we have got 68 c.c. up to 140° and 86·5 c.c. up to 170°,—

2nd. The first distillate, in this case 68 c.c., is rectified, and that which passes over up to 100° is collected, allowing the oil to drain after removing the lamp. Suppose this to be 24 c.c. This figure, multiplied by 2, gives the quantity of 50-per-cent. benzol to be expected; in this case it is 48 parts from 100 parts of the crude oil.

3rd. The product (*a*) of the first distillation (up to 140°), in this case 68 c.c., less the 50-per-cent. benzol found according to rule 2, in this case 48 c.c., gives the volume of best naphtha, *i.e.*, $68-48=20$.

4th. The total product of the first distillation up to 170°, in this case 86·5 c.c., diminished by 15 per cent. for loss by purification (washing) and distillation, and by the quantities of 50-per-cent. benzol and best naphtha found according to rules 2 and 3, gives the quantity of burning-naphtha. In this case, $86·5-13=73·5$; $73·5-68=5·5$ parts for 100 crude naphtha. (A loss of 15 per cent. may be regarded as a maximum; with careful work it does not exceed 10 per cent.)

5th. The difference is the residue going to creosote oil. Thus in our case we find the following total:—

48	parts	50-per-cent. benzol
20	„	best naphtha
5·5	„	burning-naphtha
15	„	loss
11·5	„	creosote oil
100·0		

If less volatile oils have to be tested, 200 or 300 c.c. are distilled up to 180°, and the residue is submitted to exactly the same operations and calculation-rules as have just been described.

At the present time most tar-distillers test their crude naphtha by means of fractionating-bulbs (Le Bel's, Hempel's,

etc.), and thus obtain results very nearly indicating the probable yield on the large scale (*cf.* pp. 779 *et seq.*).

Storage and Carriage of Benzol, etc.

For storing benzol and naphtha, only wrought-iron vessels are suitable; they may be of any shape and size. Since tar oils pass through the joints much more easily than water, both as liquids and as vapour, and since their vapours form with air readily inflammable or even explosive mixtures, the store-tanks must be constructed with special care and should be protected against any contact with fire. They are put together in as large plates as possible, to lessen the number of joints; and these are very carefully riveted and caulked. Only first-class workmanship will ensure that no evaporation takes place. The tanks are painted outside with good tar-varnish (pp. 441, 445), but preferably not until the joints have somewhat rusted and have thus become tighter. They are provided with a hole for filling them, a manhole, and two taps—one a little above the bottom for the ordinary filling of the sending-out vessels, the other in the bottom itself for occasionally drawing off any water and mud. The tanks are mostly placed on pillars high enough to fill the casks directly. But at some works tanks placed in the open air, and partially underground, are preferred, on account of the diminished danger of fire. In any case, for the same reason, the benzol storehouse should be at some distance from any fireplace; and it is best to employ an open shed for it. Lighting it is mostly unnecessary; in case of need, this can be done only from the outside by means of reflectors.

Hausmann (Ger. P. 90368) describes a suitable kind of reservoir for this and similar purposes. The tank B, Fig. 208, has a dome, D, and a manhole, M. From D branches off pipe R to a water-vessel, K; on the other side a back-pressure valve, V, is fixed, which allows air to get in, but no gas or vapour to escape. When B is being filled through A, the air escapes through K, where the vapours are condensed and gases escape. If they should take fire, the water-lute prevents it from being communicated to the inside of B. During the emptying of the tank, air enters gradually through V.

In order to prevent the formation of explosive mixtures of

benzol vapours and air, various inventors (as proposed first by Bunte) prescribe displacing the air in the storage vessels by carbon dioxide or gases containing a large proportion of this. Martini and Hieneke (Ger. Ps. 146161, 149086, 150712, 153703) connect the store-vessel with a reservoir for compressed air, in order to remove the benzol at once from the source of danger.

Devinet (*Chem. Zeit.*, iv., p. 219) asserts that the addition of $\frac{1}{3}$ volume of carbon tetrachloride makes benzol uninflammable in storing and using as a detergent. Pfister (*Z. angew. Chem.*, 1905, p. 1786) states that twice the volume of carbon tetrachloride of that of benzin is required for this purpose.

According to M. M. Richter (*Z. angew. Chem.*, 1903, p. 218)

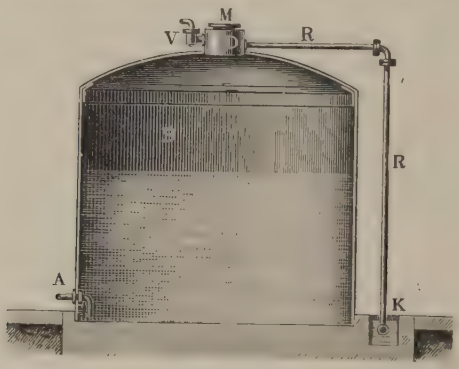


FIG. 208.

benzol is not electrically excitable, wherefore there is no danger of explosions by electric sparks occurring in its use.

Other safety apparatus for easily inflammable liquids have been constructed by Münd (Ger. P. 149924) and Schnorrenberg.

The Aktien-Gesellschaft für Anilinfabrikation at Berlin, according to *Chem. Ind.*, 1902, p. 491, has provided its benzol tanks with the safety arrangement shown in Fig. 209, which seems to be very efficient for its purpose. The tank *a* is by means of a pipe connected with vessel *b*, which is shown on a larger scale in Fig. 209*a*. *b* is divided into two chambers by a partition not reaching quite to the bottom, the opening being luted by glycerine. One chamber of *b* is connected with *a*, the other chamber with the outer air by means of pipe *c* with the cap *d*.

The latter is filled tightly with thin rods of iron, in order to prevent any flame of benzol vapours, burning at its top, from getting back into *a*.

In this connection the proposals made of issuing Rules of Safety for establishments using benzin (*i.e.*, petroleum spirits) for cleaning purposes, published in *Chem. Ind.*, 1902, p. 369, are of some interest.

Barboni (B. P. 1202, of 1905) makes benzol uninflammable by solidifying it.

Lyndall and Costley-White (B. P. 16756, 1904) aim at the same purpose by the addition of carbon tetrachloride, of which, however, too much is required to entirely remove the inflam-

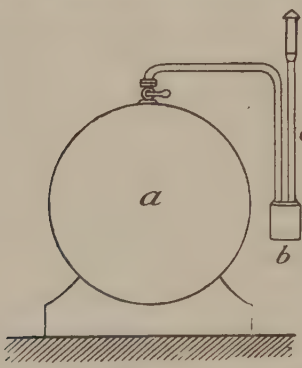


FIG. 209.

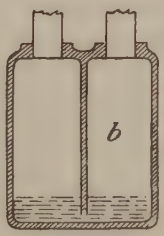


FIG. 209*a*.

mability, according to several observers. (Cf. *Chem. Zeit.*, v., p. 312, and *supra*, p. 792).

The *carriage* of benzol is effected in good oak casks, *e.g.* spirit-puncheons, preferably made tighter by washing with a dilute solution of glue, like petroleum-barrels; but tightly riveted iron casks are still better. For railway carriage, tank-waggons are very much employed.

For the momentary stoppage of leaks soap can be employed, which is not acted upon by naphtha; but it does not stand any considerable pressure. Glue, too, is not acted upon.

For *moving about benzol* at the factories, *compressed air* is very much in use as a matter of course. *Explosions*

have occurred in this process which are attributed by some to the formation of electric sparks, but it is more likely that the formation of iron sulphide from the sulphur compounds in crude benzol gives rise to such an elevation of temperature that benzol, toluol, and even higher homologues are inflamed. (*Cf.* Oehler, *Chem. Zeit.*, 28, p. 1133; Roesler, *ibid.*, p. 1237; Ernst, *ibid.*, p. 1201; Rasch, *Chem. Centr.*, 1905, ii., p. 1056.) In consequence of this, it is stated by Klocke (*Chem. Zeit.*, xxix., p. 735) that many factories have given up the use of compressed air for moving about the tar oils, but this is not necessary, if instead of common air, gases with at least 12 or 13 per cent. CO_2 (chimney gases) are employed.

Applications of Benzol and Naphtha.

Most of the benzol is employed in the manufacture of *colouring* matters, in the shape of 90-, 50-, 30-, 0-per-cent. benzol, and of nearly pure benzene, toluene, and xylenes.

Apart from colouring matters, many other technical organic preparations have a basis of benzene and its homologues, and are now synthetically produced from it. This holds good of scents, sweetening matters, and medicinal articles.

Nitrobenzene, made from the purest benzene, is sold under the name of "huile de mirbane," as a substitute for oil of bitter almonds in cheap perfumery.

Benzol also very frequently serves as *a solvent*, both in the manufacture of colours and otherwise. Of the greatest importance is its pre-eminent dissolving-power for fatty matters, upon which is based its extensive employment as a *detergent;* but petroleum "benzin" or "benzoline" largely competes with coal-tar benzol in this respect.

A good domestic detergent consists of a mixture of 25 parts benzol, 5 ether, and 5 absolute alcohol. A detergent for removing fat-, tar-, resin-, wax-, and acid-spots from all kinds of fabrics is prepared by adding 10 parts of benzol to 100 parts of 95-per-cent. alcohol, and 35 parts of liquor ammoniæ of sp. gr. 0·875. "Benzol-magnesia" (that is, burnt magnesia soaked with benzol) is excellent for removing grease-spots from fabrics, ivory, etc.

Herzfeld and Beer (Ger. P. 101414) find that an addition of 8 or 10 per cent. benzol increases the solvent power of 96-per-

cent. spirit of wine for petroleum from 10 or 12 per cent. to 20 per cent., and a further addition of 4 per cent. naphthalene brings up the solubility to 23 or 24 per cent.

Freyfs (*Chem. Zeit.*, 1903, p. 1137) reports on the application of benzol, in lieu of petroleum spirit, as a detergent, in the *Bull. Soc. Ind. Mulhouse.* He states it as an advantage of benzol that it is not electrically excitable, but as a drawback that it is injurious to the health of the workmen.

According to Russig (*Chemische Zeitschrift*, iii., p. 780), in France large quantities of solvent naphtha, boiling from 90° to 160°, are used as detergents in lieu of petroleum spirit, which is weighted by a high duty.

Baswitz (Ger. P. 127582) and Serkowski (Ger. P. 129450) employ benzolic solutions of preparations, intended for the manufacture of waterproof articles.

Benzol is used for *extracting fat* from bones and seeds, where it does $1\frac{1}{2}$ times the service of petroleum spirit, but in the extraction of seeds it has the drawback of taking up too much colouring matter at the same time.

It serves also for making *iron varnishes*, both as an addition to spirit varnishes and to the finer quality of varnishes in lieu of oil of turpentine. The Chem. Fabr. Griesheim-Elektron, according to Andès (*Chem. Centr.*, 1906, i., p. 879), has introduced turpentine, mono- and dichlorbenzene, as a perfect substitute for spirit of turpentine into the manufacture of varnishes.

In the manufacture of *indiarubber goods*, as well as in most other cases where benzol and its homologues serve as solvents, it would be too expensive, and sometimes even objectionable on account of too great volatility, to employ products consisting mainly of benzene and toluene, such as form the staple article required for colour-making. Hence the cheaper products distilling at a somewhat higher temperature, and essentially consisting of the three xylenes, along with some trimethylbenzenes, etc., are specially collected and sold as *solvent naphtha* (p. 720).

We have seen on p. 720 what are the special requirements of English indiarubber manufacturers, whose process has been described by Kniess.[1] Since it now pays to extract the xylenes for colour manufacture, the solvent

[1] *Dingl. polyt. J.*, cxxxviii., p. 442.

naphtha is of different quality to what it used to be, and such naphtha is hardly so valuable for indiarubber manufacture as the old article (*J. Soc. Chem. Ind.*, 1884, pp. 81 and 82). Heeren[1] gave a table of the solubilities of different descriptions of indiarubber in "benzol," which shows variations of from 6 to 25 parts of indiarubber to 100 of "benzol." But whether he means pure benzene, or commercial benzol, or solvent naphtha, does not appear. Ninety-per-cent. benzol serves for preparing the finest japans and varnishes, *e.g.*, for photographic purposes.

Benzol is to some extent soluble in spirit of wine of 86 volume per cent., and has hence been proposed for *denaturing spirit*, especially in the manufacture of varnishes. On diluting with water, most of the benzol separates, but the spirit retains its smell and taste. According to Kraemer, an addition of 0·1 per cent. pyridine bases is advantageous. In Switzerland solvent naphtha is used for this purpose.[2] *Cf.* also the patent of Herzfeld and Beer (p. 794).

According to tests made in the Technische Reichsanstalt (*Mitt.*, 1886, p. 11), equal volumes of yellow heavy naphtha (sp. gr. at 15° 0·887, boiling from 163° to 195°) yielded with 90-per-cent. alcohol a milky liquid, keeping most of the oil in solution and not becoming clear even on adding a great quantity of absolute alcohol. On fractionating the mixture, it was shown that the solubility in alcohol decreases with the rise of the boiling-points.

Kraemer[3] believes that a mixture of equal portions of petroleum and 90-per-cent. benzol, which dissolves even in 94-per-cent. alcohol in all proportions, should be permitted to serve as denaturing agent under the usual precautions against abuse. No less than 10 per cent. of this agent should be added to the spirit, which would prevent its being used for illegal purposes, and it would be the cheapest possible agent for denaturing.

The official prescriptions, valid in Germany since 1st October 1902, allow to employ merely $1\frac{1}{4}$ litres, *i.e.*, half of the otherwise

[1] *Dingl. polyt. J.*, ccxxi., p. 391.
[2] Lunge, *Z. angew. Chem.*, 1890, pp. 71 and 262.
[3] *Chem. Ind.*, 1899, p. 31.

necessary proportion of denaturing mixture of pyridine bases (*cf.* p. 704), if to 100 litres of alcohol 2 to 20 litres of benzol is added together with ¼ litre of a solution of crystal violet. The benzol used for this purpose, on distillation, should not yield more than 1 per cent. at 77° and not less than 90 per cent. at 100°. The smell of spirits denatured in this way is less unpleasant than that denatured in the old fashion, and it is better adapted for lighting and polishing purposes, but it burns with a rather sooty flame when using imperfect lamps.

A germicide *disinfectant* is prepared by Weyl (Ger. P. 135898) by passing gases containing ozone into benzol, heated to 60 to 70° C. This patent lapsed very soon. Russig (*Chemische Zeitschrift*, ii., p. 602) points out that according to Leeds (*Ber.*, 1881, p. 975), on passing ozone into benzol between 0° and 50 there are formed: carbon dioxide, formic acid, acetic acid, oxalic acid, and an innocuous black amorphous substance, but no phenol and no explosive substance.

The action of benzol and other hydrocarbons on microbes has been examined by Berthelot (*Comptes rend.*, vol. 137, p. 953) and Stachelin (*Chem. Centr.*, 1904, i., 1024).

Nobbe & Richter (*Chem. Centr.*, 1905, i., 116) employ benzol for sterilizing the soil, in order to obtain high crops of corn.

Xylol and cumol are employed for sterilizing catgut at 160° C. (Merck's *Jahresber.* for 1901). Beslier (*Chem. Centr.*, 1905, ii., 69) employs benzol for the same purpose.

Wolff (*Pharm. Zeit.*, 1902, 610) recommends benzol as the best agent against *lice* of all sorts.

Carburetting Gas by Tar Oils.

Both benzol and the oils distilling just after it are very well adapted for *carburetting gas*, *i.e.*, for increasing its illuminating-power by the vapours of hydrocarbons. Almost from the beginning of the coal-gas industry, inventors have been engaged in discovering a means of enriching it, by mixing it with the vapours of more light-giving substances; and the question whether this is feasible and economical is now positively decided in the affirmative.

About ten years ago the illuminating-power of gas was its only standard of value; the carburation of gas then played a very great part, and consumed large quantities of benzol, which

is most easily employed for this purpose. But since the enormous progress made by incandescent light (Welsbach mantles and their imitations), the carburation by benzol is less important, and will probably entirely cease. Water-gas, which is not an illuminant at all, gives per heat-unit a much higher efficiency with a Welsbach mantle than ordinary coal-gas, and this again a higher efficiency than oil-gas (priv. comm. by Dr Bueb).

The subject of carburetting gas has been extensively treated by Letheby,[1] Solomons,[2] Bunte,[3] Ries,[4] Stenhouse,[5] Irwin,[6] Bueb,[7] and Rau.[8] We must refer the reader to these papers, and to those which have appeared afterwards in such numbers that we must abstain from going further into them.

Dr Letheby's specification, which was adopted by the London lighting authorities (p. 719), must yield a product essentially consisting of xylene. He did not assume this to act better than benzene or toluene; but he selected that product because it was not then employed at colour-works, and consequently was lower in price. By Knublauch's investigations[9] it has been ascertained that, in fact, benzene, for equal weights, imparts the greatest illuminating-power to gas, and that the higher homologues act only in proportion to their molecules, only the carbon of the benzene nucleus being set free in a luminous form, whilst that of the methyl groups is burned directly to carbon dioxide. Formerly it seemed out of the question to employ benzene itself for carburetting either coal-gas or air (although the first person who manufactured benzene on an industrial scale, Mansfield, had the latter object in view), as the high value of benzene was an impediment to such an employment; but at the present prices benzene (*i.e.*, 90-per-cent. benzol) is quite cheap enough for this purpose.

It is well known that gas, when being passed in a continuous stream through a liquid containing several volatile substances of different boiling-points, will in the first instance carry away

[1] *Chem. News*, xi., p. 276.
[2] *J. Gasbeleucht.*, 1892, p. 5.
[3] *Ibid.*, 1893, p. 442.
[4] *Ibid.*, 1894, p. 1.
[5] *J. Soc. Chem. Ind.*, 1895, p. 435.
[6] *Ibid.*, 1895, p. 546.
[7] *Z. angew. Chem.*, 1895, p. 622.
[8] *Die Aufbesserung des Leuchtgases mit Benzol*, 3rd ed. (Kattowitz, 1895).
[9] *Berl. Ber.*, 1881, p. 240.

a larger quantity of the more volatile portions, and that the composition of the remaining liquid must consequently undergo constant changes. This is a drawback to all carburetting liquids, but much less to a liquid approaching pure benzene, such as commercial 90-per-cent. benzol, as they are all such compound substances. Thus carburetting naphtha made according to Letheby's specification, in experiments made by G. E. Davis,[1] yielded at first 3·25 gallons of the lighter oils to 10,000 cubic feet of gas, but after a time scarcely anything was vaporized, and the boiling-points of the remaining naphtha were much higher. Exactly the same thing occurred with 50- to 90-per-cent. benzol, and even with 90-per-cent. benzol (which under similar circumstances yielded about 15 gallons to 10,000 cubic feet of gas). The same happens with gasoline and other mixtures of fatty hydrocarbons. The irregular evaporation of the fluid is a serious drawback in the case of all mixed liquid, but it would not apply to a uniform substance like naphthalene. Davis found that the residual fluids contained in absolute quantities more of the higher-boiling hydrocarbons than originally; evidently the gas took up the benzene by preference, and deposited its own hydrocarbons of lower vapour-tension in the carburetting-fluid, thus making it still more unsuited for enriching the gas.

The carburation takes place either at the burner itself or at the gas-works. In the former case it is troublesome to constantly replenish the reservoirs with the carburetting-liquid. There is rather less trouble in this respect, but more in others, in the case of naphthalene, as described, p. 658. The apparently easier plan of carburetting at the gas-works involves the necessity of so treating the mixture that the gas may not deposit the carburetting-substances on its way through the network of pipes. The American water gas-works therefore "*fix*" the carbon of the hydrocarbon vapours mixed with the water-gas by passing the mixture through red-hot retorts, or in some similar manner. In this process, no doubt pyrogenetic changes are effected similar to those described, pp. 141 *et seq.* When carburetting gas with low-boiling benzol, such "fixing" is not necessary; the methane present in the gas seems to render the benzene-vapour more stable as such.

[1] *J. Soc. Chem. Ind.*, 1886, p. 4.

The quantity of benzol required for carburetting coal-gas differs from 2 to 4 g. per hour and candle. The foundation for judging of this is the fact, established by Bunte, that normal coal-gas contains 43 g. per cubic metre. The "mixed gas," recently very much in use, consisting of $\frac{2}{3}$ water-gas + $\frac{2}{3}$ coal-gas, requires the addition of 40 g. benzol per cubic metre to attain a power of 16 candles. Sospicio states the quantity required for a mixture of $\frac{1}{3}$ water-gas + $\frac{1}{3}$ coal-gas = 23 g. for 16 candles.

Benzol seems to be eminently adapted for carburetting water-gas, such as is obtained in the Dellwik-Fleischer apparatus. According to Dicke, Wahl, and Bueb (*J. Gasbeleucht.*, 1903, pp. 411 and 900), good progress seems to be made in this direction.

It has been contended that benzol, when applied to carburetting gas, destroys the dry gas-meters. This is contradicted by Witzek (*J. Gasbeleucht.*, 1904, 656) and by Messerschmidt (*J. Gasbeleucht.*, 1906, p. 235).

The price limit at which carburation of gas by means of benzol is still paying, according to Bunte, is at 40 mark, according to Kraemer at 50 mark per 100 kg.

The *valuation of tar oils for the process of carburetting water-gas, etc.*, is treated by Spiegel (*J. Gasbeleucht.*, 1907, p. 45) *J. Gas Lighting, Water Supply, etc.*, 1907, p. 822). The ordinary tests do not indicate their value for that purpose, nor does the calorific test, since oils which are not sufficiently volatile to be taken up by cold gas are useless in this case, and so is naphthalene. Hence, many gas engineers trust only to practical trials on a large scale. Spiegel asserts that an oil is all the more valuable as carburetter the more nearly saturated its hydrocarbons are. He therefore determines the proportion of hydrogen in it by the ordinary process of ultimate elementary analysis. He describes a way of calculating from this the carburetting value of the oils, but since he confines this to the heavy oils used for carburetting water-gas by the hot process, not to those which are employed in the cold, and since he himself admits that further experiments are necessary for comparing his data with the results obtained on the large scale, we must refer the reader to the original.

Employment of Naphtha and Benzol for illuminating purposes.

The highest boiling oils obtained by the steam rectification, if they cannot be worked in with solvent naphtha, are sold as *burning-naphtha*. Coal-tar naphtha, whether pure or mixed with petroleum spirit, is not adapted for burning in ordinary lamps or at all in closed rooms, but merely for special lamps, without wick or chimney, which burn well even in strong wind and rain, and hence serve for lighting factories, courtyards, booths at fairs, etc., in lieu of gas. Good naphtha, no doubt, gives a very fine white light. Figs. 210 and 211 show a suitable lamp for this

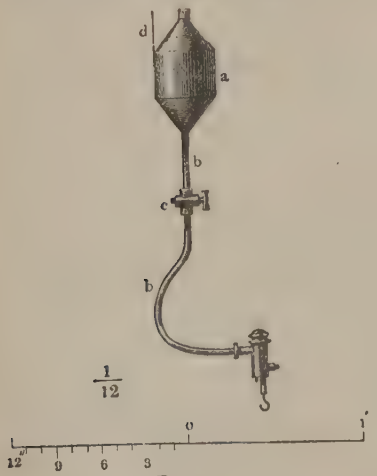


FIG. 210.

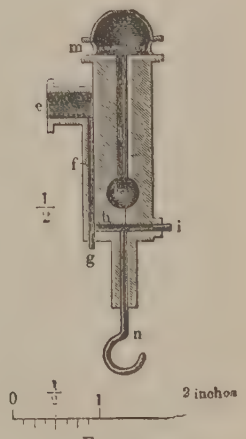


FIG. 211.

purpose (Holliday's patent). Fig. 210 is the lamp itself, on a scale of 1 : 12; Fig. 211, the burner, on a scale of 1 : 2. *a* is the reservoir for naphtha, from which a thin tube *b* leads downwards; the cock *c* regulates the outflow; the tube *b* is almost entirely filled up by a round wick which extends nearly to the burner, and the sole purpose of which is to make the outflow of the naphtha gradual. The hook *d* serves for hanging up the lamp. In the burner we notice the lateral tube *e*, communinating with *b*, and introducing the naphtha. This flows downwards in the narrow channel *f*, which is closed by the thin screw *g*, the channel *h* being closed by *i*. The naphtha must rise from *h* in the fine central channel, leading to a hole, *k*, across

the burner. Here it would run off if the burner had not been previously heated sufficiently to evaporate it at once. The vapour mixed with the air entering at *k*, rises in the central channel *l*, issues through the holes in the burner-head, and, on being lighted, produces a star-shaped flame. The draught generated by this suffices for preventing the naphtha-vapour from issuing into the open air instead of into the channel *l*. The screw *n* permits regulating the orifice of the fine channel between *h* and *k*. Here also a small cup may be fixed for some naphtha to be lighted in order to effect the first heating of the burner, the tap *c* being then closed. Otherwise the burner-head is put into a fire till it is warm enough. When this is the case, the tap *c* is opened, the vapour issuing out of the holes *m* is lighted, and the size of the flame regulated by *c*. Once lighted, the burner always remains warm enough.

When burning-naphtha can be sold in quantity, it is advisable to mix it with *petroleum spirit*, which in this case is an improvement, and especially tends to keep it colourless. The petroleum spirit can be pumped into the still after the solvent naphtha has come over, and can be distilled along with the burning-naphtha. Care should be taken that about equal parts of coal-naphtha and petroleum spirit distil together; the smell of the latter will then be imperceptible. Or else the petroleum spirit is mixed with the naphtha after distillation. The best descriptions of petroleum-spirit for this purpose are those which give off very little below 100°, but nearly the whole up to 170°.

Since the recovery of benzol from coke-oven gases has immensely increased the available quantity of this article, it is of course a most momentous question for the tar-distillers to find fresh outlets for it; and there are prospects for employing benzol as an illuminant, to replace petroleum at least partially. Kraemer (*Chem. Ind.*, 1899, p. 32) finds that a mixture of 4 parts benzol, 4 petroleum, and 6 96-per-cent. spirit answers very well for *incandescent lamps*. The mixture has the same illuminating-power as petroleum itself, but 20 per cent. more is consumed of it than of pure petroleum. Russian petroleum serves even better than American for this mixture, which at the present prices of benzol and spirit, would already pay, but would be more remunerative if the price of petroleum were to be raised to any considerable extent.

A mixture of 47 volumes of "technical benzol" (consisting of about 95 benzene + 5 toluene, and yielding at least 90 per cent. up to 90° C.) with 15 volumes solvent naphtha (yielding 90 per cent. up to 175°) and 38 volumes spirit-of-wine (94 per cent.) which solidifies only at −17° C., is very well adapted for street lamps. If burnt in an ordinary flat burner, 50 to 61 g. per hour are required for an illuminating power of 17 to 19 candles per hour.

"Carbosprit" is a mixture of 40 spirit-of-wine with 60 benzol, employed for incandescent lamps by W. v. Cnobloch (*J. Gasbeleucht.*, 1902, p. 194).

Plehn (Ger. P. 156988) makes an illuminating liquid from 70 to 95 volumes of 90-per-cent. spirit-of-wine + 5 to 30 volumes of purified "solvent naphtha" (p. 720), boiling between 160° to 180° C. This mixture burns in an ordinary lamp, provided with a wick without any coat, and is to be used in the place of petroleum.

The firm Denayrouze has constructed an elegant benzol lamp for use in dwelling-rooms, equal to any lamp for petroleum spirit. It is stated that 5 g. of the benzol, called "lusol" by that firm, suffices for 1 candle-hour.

Benzol is also used as an addition to "solidified spirit-of-wine" for heating and lighting purposes (*Pharm. Zeit.*, 1902, 318).

W. van der Heyden (Ger. P. 176366) *solidifies* benzol (as well as petroleum or petroleum benzin) by mixing it with glue, made into a jelly or dissolved in water, and drying or hardening the glue by formaldehyde.

Other Uses of Benzol.

A new use of benzol has been found for *driving motors* and *motor cars*, in lieu of petroleum-spirit. For this purpose the "technical benzol" just mentioned, consisting of about 95 benzene + 5 toluene is used, especially for motors with electrical inflammation and pre-heating. The motors of the Cologne-Dentz and some other works consume of that benzol on an average 350 to 400 g. per h.p. hour—that is, from 50 to 100 less than of petroleum-spirit. For motor cars a mixture of 80 parts spirit-of-wine and 20 benzol is said to have answered very well. A number of statements on this use of benzol is collected in *Chem. Zeit.*, 1908, pp. 114 and 115, and in a paper by Hönigsberger (in *Z. angew. Chem.*, 1909, p. 671).

Mixtures of benzol with spirit-of-wine, sometimes sold by

the name of *ergine*, are now frequently used for explosion-motors. *Cf.* on this Kraemer (*Z. Verein. deutsch. Ingen.*, 1906, p. 522); W. A. Th. Müller (*ibid.*, 1903, p. 59); Eugen Meyer (*ibid.*, 1903, p. 632).

Soot is to be produced from benzol, according to Thalwitzer (Ger. P. 109826), by burning it, mixed with gases of low value.

Sydney Young (*Proc. Chem. Soc.*, xviii., p. 104; *Chem. Centr.*, 1902, i., 1317) makes *absolute alcohol* by several times fractionating a mixture of spirit-of-wine with benzol. The traces of benzol remaining in the alcohol are to be removed by a special process, hardly fit for technical use. This process is the subject of Ger. P. 142502.

Darmstaedter (Ger. P. 125404) employs toluol to form an emulsion in order to obtain smooth precipitates in *electrolytic baths*.

Bunte & Eitner (*Chem. Zeit.*, 1889, rep. 53 and 216) employ solvent naphtha for removing the naphthalene from gas-pipes. Breitkopf (*ibid.*, p. 319) found this very efficient.

Of other applications of benzol we will mention that for extracting iodine[1] (which has hardly ever been practised), in making beetroot sugar,[2] and as a remedy for eruptions of the skin, itch, and parasites of domestic animals (in the shape of a mixture with soft soap).

Statistics of Benzols.

The productive capacity of the United Kingdom for benzol of various types was estimated by Levinstein (*J. Soc. Chem. Ind.*, 1886, p. 351) for the year 1886 at nearly 3 million gallons, of which quantity Germany took 1½ millions (in addition to ½ million home production), England ½ million, France and other countries the remainder.

Germany, during the years 1870 to 1880, produced only about 1200 tons per annum; 1890, already about 4000 to 5000 tons; 1896, 7000 tons; 1901, 25,000 to 30,000 tons; 1904, 36,000 to 38,000 tons. In 1906 the Rhenish-Westphalian provinces alone produced nearly 40,000 tons of benzols, so that the German colour-works, which formerly had to get about ⅞ of the benzol they required from Great Britain, now get it nearly all in Germany. If all the coke in that country was made by recovery-ovens, she would produce upwards of 70,000 tons, which is far above the

[1] *Wagner's Jahresber.*, 1886, p. 182. [2] *Ibid.*, 1874, p. 674.

quantity now saleable at present or in a near future. Indeed, during the last few years a good many new coke-ovens have been built in Germany on the old place, as there was not enough chance for selling the products made by recovery-ovens.

Fluctuations in the Prices of Benzol.

The following diagram, Fig. 212, by Kraemer, shows the fluctuations of the prices of benzol during the years 1891 to 1898, the perpendicular lines indicating the shillings and pence per gallon.

F. Frank (*Chem. Ind.*, 1901, p. 238) quotes the following prices

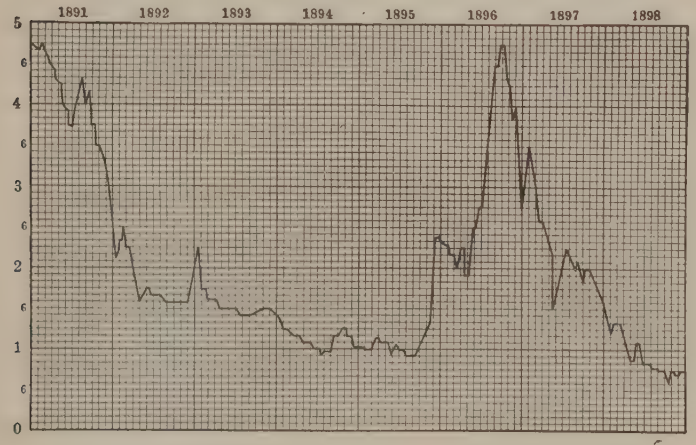


FIG. 212.

per 100 kg. of benzol (what strength?) in Germany, which also clearly show the influence of the recovery of benzol in the manufacture of coke, as well as the previous violent fluctuations.

Year.	Mark.	Year.	Mark.
1882	175 to 400	1897	65
1885	50 „ 90	1898	25
1890	100 „ 125	1899	20
1892	40 „ 60	1900	20
1895	25 „ 60	1901	30
1896	50 „ 120		

Since 1902 the price has been from 20 to 21 mark per 100 kg.

Russig, in his various reports on coal-tar products in the

Chemische Zeitschrift, gives the following statistics for the importation and exportation from Germany (the figures denote metrical tons, at 1000 kg.).

Imported.

Year	1899.	1900.	1901.	1902.	1903.	1904.	1905.
Sulphate of ammonia	28,808	23,105	44,407	42,251	35,168	35,165	48,005
Gas-liquor	21,504	26,407	13,765	10,267	(?)	(?)	(?)
Anthracene	4,305	3,894	3,296	2,876	2,048	1,230	1,350
Carbolic acid and other phenols	3,908	4,225	4,538	5,154	5,016	5,266	5,536
Naphthalene	3,776	9,802	12,596	11,464	14,481	12,444	11,645
Coal-tar oils, light	5,291	7,210	7,723	7,591	8,063	5,779	8,104
Coal-tar oils, heavy	2,543	3,286	9,267	6,800	6,579	5,608	7,265
Tar of all descriptions	39,696	35,553	37,508	40,574	36,788	40,641	37,292
Pitch, asphalt, wood-cement[1]	61,534	80,765	62,299	88,536	94,377	85,049	82,461

Exported.

Sulphate of ammonia	1,553	2,431	9,842	5,744	5,592	10,696	27,589
Gas-liquor	16,971	17,068	15,400	15,857	(?)	(?)	(?)
Anthracene	...	...	1	154	1	49	13
Carbolic acid and other phenols	2,850	2,452	3,198	3,357	3,102	3,898	5,275
Naphthalene	1,270	1,274	1,261	2,455	2,333	2,878	2,735
Coal-tar oils, light	2,755	2,994	2,260	2,222	2,982	4,390	6,560
Coal-tar oils, heavy	8,640	10,506	5,992	5,704	8,596	12,982	23,292
Tar of all descriptions	30,678	32,437	31,433	29,818	31,898	32,872	42,889
Pitch, asphalt, wood-cement[1]	37,771	36,921	39,670	40,595	49,785	55,359	62,040

[1] How much of this is coal-tar pitch cannot be ascertained.

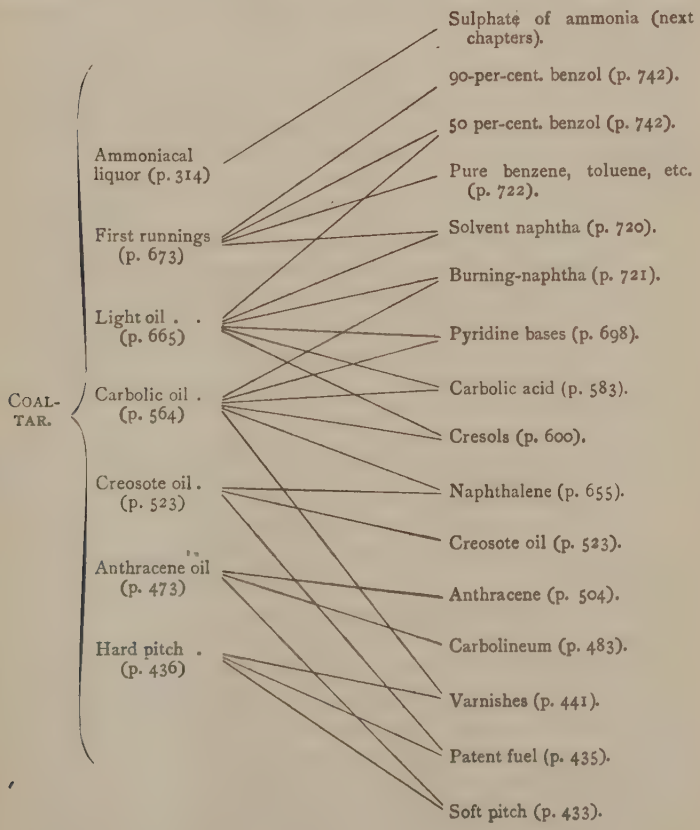
In the year 1906 a new tariff and new designations were introduced in the German Customs Union, and for this year no useful statements can be made. For 1907 the following figures can be given for the importation and exportation into and from Germany:—

	Imported. Tons.	Exported. Tons.
Coal-tar	29,276	32,062
Coal-tar pitch	20,283	16,892
Benzol (from coal-tar)	4,114	1,681
Toluol, cumol, and other light coal-tar hydrocarbons	5,683	3,394
Heavy coal-tar oils and asphalt-naphtha	7,034	50,802
Naphthalene	10,144	5,980
Anthracene	2,418	32
Phenol, crude and pure	5,277	3,561
Cresol	3	410
Sulphate of Ammonia	33,522	57,493

APPENDIX I

Synopsis of the Products obtained from Coal Tar.

In conclusion we give a synopsis of the Products obtained from coal tar, with enumeration of the final products and the pages where a description of the respective substances is to be found :—


Coal-tar.
Ammoniacal liquor (p. 314)
First runnings (p. 673)
Light oil . . (p. 665)
Carbolic oil . (p. 564)
Creosote oil . (p. 523)
Anthracene oil (p. 473)
Hard pitch . (p. 436)
Sulphate of ammonia (next chapters).
90-per-cent. benzol (p. 742).
50 per-cent. benzol (p. 742).
Pure benzene, toluene, etc. (p. 722).
Solvent naphtha (p. 720).
Burning-naphtha (p. 721).
Pyridine bases (p. 698).
Carbolic acid (p. 583).
Cresols (p. 600).
Naphthalene (p. 655).
Creosote oil (p. 523).
Anthracene (p. 504).
Carbolineum (p. 483).
Varnishes (p. 441).
Patent fuel (p. 435).
Soft pitch (p. 433).

APPENDIX II

Official Recommendations to prevent Accidents in Tar-distillation Works.

The following rules were issued in 1903 by the Home Office, consequent upon a report by the Inspectors of Factories, eleven fatal and ten non-fatal accidents having occurred within three years, mostly ascribed to the inhalation of sulphuretted hydrogen. Those specified in paragraph (2) are specially important.

(1) All uncovered tar reservoirs, wells, and tanks, unless constructed so as to be at least 3 feet in height above the ground or platform, should be securely fenced with either a brick wall or double rail, to the height of 3 feet.

(2) During the process of cleaning, every tar-still should be completely isolated from the adjoining tar-stills, either by disconnecting the pipe leading from the swan-neck to the condenser worm, or by disconnecting the waste gas-pipe fixed to the worm end or the receiver. Blank flanges should be inserted between the disconnections. In addition the pitch discharge-pipe at the bottom of the still should be disconnected.

(3) Every still should be ventilated and allowed to cool before persons are allowed to enter.

(4) Every tar-still should be inspected by the foreman or other responsible person before any workman is allowed to enter.

(5) No person or persons should be allowed to enter a tar-still, or tank, unless provided with a belt securely fastened round the body with a rope attached, the free end to be left with two men outside, whose sole duty should be to watch and draw out any man in the tank who should appear to be affected by gas.

(6) A bottle of compressed oxygen, with mouthpiece, should be kept at all times ready for use, and printed instructions as to the use of the bottle, and the methods to be employed for resuscitation by means of artificial respiration, should be kept constantly affixed. A draft of such instructions is appended.

(7) A supply of suitable chemical respirators properly charged and in good condition should be kept ready for use in case of emergency arising from sulphuretted hydrogen or

certain poisonous gases. (Granules of carbon saturated with a solution of caustic soda readily absorb sulphuretted hydrogen, and may be used for charging respirators.)

(8) The use of naked lights should be strictly prohibited in any portion of the works where gas of an inflammable nature is liable to be given off.

(9) Each still should be provided with a proper safety-valve, which should at all times be kept in efficient working condition.

CHAPTER XII

SOURCES FROM WHICH AMMONIA IS OBTAINED

Historical Notes.

THE word "ammonia" occurs in two entirely different meanings. With one of these, the "gum ammoniac" (which is a kind of resin obtained from an umbelliferous plant growing in abundance near the temple of Jupiter Ammon, in Egypt), we have nothing to do here. The other meaning of "ammoniakon" or "sal ammoniacum," is that which we now connect with the word "sal-ammoniac," *i.e.*, ammonium chloride. The word ammoniakón[1] occurs in the first meaning already in the writings ascribed to Hippocrates, and dating from the fifth century before Christ; also in those of Pliny, Dioscorides, and other authors of the classical times, as well as later on in the writings of mediæval Arabians and Europeans. Herodotus speaks of "hals ammoniakos," *i.e.*, ammoniacal salt, but he evidently means the crystallized *rock-salt* (sodium chloride) of the Ammonian Oasis, and so do all the following Greek and the later Syrian and Arabian authors, up to the sixth century of our era.

In the second meaning, that which *we* give to the word "sal-ammoniac" (ammonium chloride), we find that word in Pliny, who rather indistinctly speaks of it as sometimes occurring in Egyptian "nitron" (natural soda). But a more accurate knowledge of it dates only from the development of the processes of sublimation and distillation in Egypt, say, about the fourth century after Christ, since it was evidently observed when burning camel dung in fireplaces provided with a chimney. The Arabian polyhistor, Al-Gariz (deceased in

[1] We follow here the statements of E. O. von Lippmann, in *Chem. Zeit.*, No. 14, of 1909.

869 A.D.), mentions sal-ammoniac as one of the matters well known to have been obtained by the Arabs from the Greek, by the Persian name "nashadir," which is found in various other Arabian and Persian authors later on. As "sal armoniacum," our sal-ammoniac is first mentioned by the European chemists of the twelfth century, and frequently in the sixteenth and seventeenth centuries, either in that form or in that of "sal ammoniacum." Glauber already knew that it can be artificially obtained by the combination of muriatic acid with the "volatile alcali" expelled by lime from sal-ammoniac, which was known already to Raymundus Lullus in the thirteenth century. Kunckel in the "Laboratorium chymicum" (1700) compares this "volatile spirit of sal ammoniacum" with caustic-alkaline liquors, but it was left to Priestley, in 1774, to discover the pure ammonia gas, by collecting it over mercury when decomposing sal-ammoniac with lime. He designated it as "alkaline air"; the designation "ammoniacum" or "ammoniá" was given to it in 1782 by Bergman Berthollet, who in 1785, and more explicitly in 1809, showed its composition from nitrogen and hydrogen in the now well-known proportions by decomposing NH_3 by means of the electric spark.

Sources from which Ammonia is Obtained.

Ammonia is formed in many cases where nitrogen and hydrogen meet in the nascent state, even when only one of these substances is in that state. Thus, for instance, ammonia is formed by passing a mixture of hydrogen and "nitrous vapours" (*i.e.*, a mixture of the oxides of nitrogen) through a gently heated tube, filled with porous substances, especially platinum sponge. Cold platinum sponge becomes heated to redness in such a mixture, and causes the combination of N and H to NH_3 with great violence. Especially nascent hydrogen causes the formation of ammonia from nitrates and nitrites, also from the free acids, but best in alkaline solution, when the hydrogen is set free by aluminium or a mixture of zinc and iron. Iron in a very finely divided state (as "ferrum redactum") reduces nitrates quantitatively to ammonia in a solution containing sulphuric acid, upon which reaction Ulsch[1] has founded an excellent analytical method. In concentrated solutions iron

[1] *Z. anal. Chem.*, xxx., p. 75.

alone causes also the decomposition of nitrates in the presence of alkali.[1] Sodium sulphide in the presence of sodium hydrate also furnishes ammonia by heating with nitrate; the conditions of this reaction, a very important one in the manufacture of caustic soda, have been accurately investigated by Lunge and J. H. Smith.[2]

Atmospheric nitrogen, according to Schönbein, directly unites with the elements of water and forms ammonium nitrite,

$$2N + 2H_2O = NH_4NO_2;$$

this reaction occurs, to a slight extent, every time when water evaporates with excess of air. The combination of free nitrogen and hydrogen is accelerated by the electric spark or the silent electric discharge, but it is always very far from being complete, as the counter-reaction of decomposing the NH_3 into its elements very soon sets in. Loew (*Berl. Ber.*, 1890, p. 1443) observed that atmospheric nitrogen in the presence of caustic soda is converted by potassium back into nitrous acid and ammonia.

We may observe at once that no economical and technically available process has been found as yet for utilizing the direct union of nitrogen and hydrogen to produce ammonia on a manufacturing scale.

Ammonia is further formed by the decomposition of cyanogen compounds under the influence of moisture. A solution of potassium cyanate is quickly decomposed in this way:

$$KCNO + 2H_2O = KHCO_3 + NH_3.$$

The cyanides also yield their nitrogen in the shape of ammonia in contact with superheated steam; several processes for technically obtaining ammonia are founded on this reaction.

In the economy of nature, the formation of ammonia during the decay of nitrogenous organic substances is the most important source of that compound—all the more as the naturally occurring nitrates are undoubtedly for the most part formed by the oxidation of such ammonia. The formation of ammonia is most easily understood in the decomposition of urea, which, being the amide of carbonic acid, needs only to

[1] Lunge, *J. Soc. Chem. Ind.*, 1884, p. 287.
[2] *J. Soc. Chem. Ind.*, 1883, pp. 460 and 525.

combine with water in order to pass over into ammonium carbonate,

$$CO(NH_2)_2 + 2H_2O = CO_3(NH_4)_2.$$

But the other organic substances in the course of putrefaction also yield part, or sometimes the whole, of their nitrogen in the shape of ammonia.

For technical purposes it is most important that nitrogenous organic substances, when heated in the absence of air, that is in destructive distillation, also yield their nitrogen, at least partly, in the shape of ammonia. Although animal matters contain much more nitrogen than vegetable ones, it is a derivative of the latter, namely coal, which supplies most of the ammonia used in the arts and manufactures, when subjected to destructive distillation for the purpose of obtaining illuminating-gas and coke. But probably a very large portion of the nitrogen in coal is due to the animal remains buried in it, and to atmospheric ammonia absorbed, as we shall see later on.

We shall now treat separately of the various technical sources of ammonia.

A. Natural Occurrence of Ammonia.

Ammonia, especially as carbonate, is found almost everywhere in soil, water, and air, as a product of the decomposition of organic bodies, but in very slight traces. Although the growth of plants seems altogether to depend upon the ammonia thus presented to them and upon the nitrates formed by the oxidation of that ammonia (along with that formed by the electric discharge); yet this ammonia is diluted to such an enormous extent that it will ever be out of the question to recover it in substance.

In some cases rather more ammonia is collected in one spot, owing to the absorptive faculty of some kinds of clay, of peat, etc. But even in such cases it would seem hopeless to recover it in a direct way, although this sometimes becomes possible indirectly, when the materials in question are subjected to processes for recovering other useful substances, *e.g.*, peat to dry distillation, for the purpose of extracting oils and paraffin. Indeed the principal source of ammonia, coal, seems to owe its nitrogen in a great measure to the absorptive faculty of some

forms of decaying organic matter for the ammonia of air, and of that produced within its own mass.

A more direct opportunity of recovering ammonia is presented when, under favourable circumstances, the ammonium salts formed in the decomposition of organic matter are not, as is usual, at once diluted and dispersed, but are allowed to collect and concentrate. Thus ammonium carbonate in substance is found in the *guano deposits* on the west coast of South America, sometimes in such large quantities that it can be exported to Europe. Such ammonium salt first appeared in Germany in 1848. The analysis of a sample proved that it consisted essentially of ammonium bicarbonate, mixed with some insoluble matter.

Native ammonium sulphate is contained in the Tuscan "*suffioni*," and forms a by-product in the manufacture of boric acid. It is also found in large quantities in the soil surrounding the lagoons, and may have been produced by decomposition of nitrogenous organic matter in the rocks composing the Tuscan hills. In an experiment made at Travale, four suffioni in 24 hours yielded 5 tons of salts, containing 3 cwt. boric acid, $1\frac{1}{2}$ tons of ammonium sulphate, $1\frac{3}{4}$ tons of sulphate of magnesia, and $\frac{3}{4}$ ton of sulphate of iron and manganese. Somewhat considerable quantities of ammonium sulphate are brought into the market from this source.

Native ammonium chloride, along with sulphate, is sometimes collected in the neighbourhood of *volcanoes*, as Vesuvius and Etna. This occurrence is never of any importance; but it is asserted that the name "ammoniac" is derived from "sal armeniacum" or "armoniacum," that is, sal-ammoniac collected at the Armenian volcanoes. Since, however, the Arabian chemist Geber, as early as the eighth century after Christ, prepared sal-ammoniac from urine and common salt, in the way it is done even now in the East, it would seem very doubtful whether sal-armoniacum should be looked upon as a volcanic product.

The carnallite of Stassfurt contains ammonium chloride, sometimes as little as 0·015 per cent., but sometimes several per cent. The newest paper on this occurrence is by Biltz and Marcus (*Z. anorg. Chem.*, 1909, lxii., p. 183). Diehl,[1] Neimke,[2]

[1] *Chem. Zeit.*, 1889, p. 64. [2] *Ibid.*, 1891, p. 715.

Tröger, Stolle,[1] and Vogel[2] found ammonium chloride in several descriptions of rock-salt. Friedel and Pisani[3] found in apophyllite 0·33 to 0·51 ammonia, and Lüdecke confirmed this for another description of that mineral. Erdmann[4] found ammonia in the oldest rocks of Finland and Scandinavia: he believes that this nitrogen, contrary to that in carnallite, etc., is not of animal origin, but is "original nitrogen" (Urstickstoff), which must have played a great part in the development of vegetation, and is probably doing so even at the present time.

In any case a very small proportion of the ammonium salts occurring in commerce is derived from native sources.

B. Ammonia formed from the Nitrogen of Atmospheric Air.

It is a well-known fact (*cf.* p. 812) that ammonia can be formed directly from its elements, more especially by the electric discharge;[5] also in the process of combustion of a mixture of hydrogen, oxygen, and nitrogen (Saussure). But in both cases the inverse reaction, that is, the decomposition of ammonia by heat and electricity, is far more powerful (*cf.* later on); so that it seems a hopeless task to manufacture ammonia directly from atmospheric nitrogen, unless some special agency can be found which favours the formation and suppresses the decomposition of ammonia. Very confident assertions have been made from time to time in this respect by various inventors, but nothing useful has followed. The small quantities of ammonia, *bonâ fide* obtained in the experiments, may sometimes have been pre-existent in the materials employed; and so much is certain, that none of it has ever been brought into commerce. This has been once more stated by Truchot at the International Congress for Applied Chemistry in 1898.[6]

We may, with L. Mond,[7] divide the processes of this kind into three classes:—

1. Processes which aim at the combination of nascent

[1] *Z. angew. Chem.*, 1891, p. 625. [2] *Ibid.*
[3] *Bull. Soc. franç. de Minéral.*, 1894, p. 142.
[4] *Berl. Ber.*, 1896, p. 1710.
[5] *Cf.* Donkin, *Proc. Roy. Soc.*, vol. xxi., p. 281.
[6] *Z. angew. Chem.*, 1898, p. 263. [7] *J. Soc. Chem. Ind.*, 1889, p. 505.

hydrogen with nitrogen at high temperatures, or with the assistance of electricity, or in the presence of acid gases.

2. Processes in which primarily nitrides are formed which are afterwards transformed into ammonia.

3. Processes in which primarily cyanides are formed.

(Those processes in which ammonia is made from atmospheric air with the concurrence of peat will be described lower down in section H.)

1. *Application of High Temperatures, Contact Substances, Electricity, etc.*

H. Fleck[1] describes the following experiment. When hydrate of lime is brought to a red-heat, its chemically combined water is split off, and in this state is more prone to be decomposed. If, therefore, a mixture of nitrogen and carbon monoxide is present at the same time, the following reaction takes place:—

$$2N + 3CO + 3H_2O = 2NH_3 + 3CO_2.$$

This reaction was utilized by passing atmospheric air over charcoal contained in an iron tube heated to a red-heat; the issuing gas was passed through boiling water, and then through a porcelain tube filled with hydrate of lime. Whenever the latter tube was heated to a temperature "between dark red and bright red," considerable quantities of ammonia were formed (in one case 16 grains NH_4Cl from 15 cubic feet of air); but a little above or below that temperature the evolution of ammonia was very slight, or ceased altogether. Fleck himself published his experiments only as a stimulus for further trials. Weinmann,[2] on repeating Fleck's experiments, could not obtain any ammonia; but this may have been due to his not having hit the precise temperature required; nor was Mond (*loc. cit.*) more successful.

Maxwell Lyte[3] passes a mixture of steam and nitrogen over certain alloys or other compounds of the metals of the alkalis or the alkaline earths, or zinc, namely, alloys of antimony, bismuth, arsenic, or tin with sodium, potassium, or zinc. The hydrogen liberated is supposed to unite with the nitrogen and to form ammonia.

[1] *Die Fabrikation chemischer Produkte aus thierischen Abfallen* (Braunschweig, 1862), p. 48.

[2] *Ber.*, 1875, p. 977.

[3] *Bull. Soc. Chim.*, 1876, xxv., p. 427.

Ed. Solvay[1] impregnates coke with magnesium chloride and heats the mixture by means of a blast. The products of combustion contain sal-ammoniac, which is to be recovered by condensation. The priority of this invention is claimed by R. Wagner.[2] Probably any ammonia formed in Solvay's experiments was derived from the nitrogen contained in coke (*cf.* later on).

G. Swindells (B. P., June 21, 1876) passes a mixture of air and steam over red-hot coals, and the resulting mixture of gases through a solution of caustic soda. The escaping mixture of hydrogen and nitrogen is to be converted into ammonia by heating in chambers filled with burnt clay. [In all likelihood the ammonia found by Swindells was likewise formed from the nitrogen of the coal.]

J. P. Rickman (B. P. 3341, of 1878) employs slanting retorts, made of iron or fireclay, of an elliptical section, filled with coke or spongy iron, and heated to about 550° C. At the lower end a mixture of steam and air is blown in; the steam is decomposed, and the free hydrogen combines with the nitrogen to form ammonia, which issues at the upper end of the retort, mixed with the excess of steam.

A modification of this proposal was patented by J. P. Rickman along with J. B. Thompson in 1880 (Ger. P. 10889). They expose coal to a slow combustion with access of air and steam in regulated quantities.

G. Th. Glover (B. P. 1890, of 1880) passes combustion-gases, containing much nitrogen, mixed with steam and hydrochloric acid, over red-hot coals or bituminous shale. The ammonium chloride formed is to be condensed by cooling, or is passed into sulphuric acid.

To the proposals of Rickman, Thompson, and Glover, we must apply exactly the same observation as to that of Swindells. Mond (*loc. cit.*, p. 815) confirms the statement that any ammonia obtained in these cases comes from the nitrogen originally present in coal.

H. Endeman (*Amer. Chem. J.*, vol. viii., p. 47) observed the occurrence of ammonium thiosulphate as a condensation product from a gas-producer in which a mixture of air and

[1] *Bull. Soc. Chim.*, 1876, xxv., p. 527.
[2] *Jahresb. f. chem. Technol.*, 1876, p. 444.

steam was forced through anthracite coal, and he believes that the sulphur was derived from the anthracite coal, the nitrogen from the atmospheric air, and the hydrogen from steam. There is, however, no proof whatever given that the coal did not contain sufficient N to account for the NH_3 formed.

G. S. Johnson[1] asserts that ammonia is formed if nitrogen, prepared by gently heating a mixed solution of potassium nitrite and ammonium chloride, is mixed with hydrogen and the mixture is passed over red-hot platinum sponge; or else if such nitrogen is passed over cold platinum sponge charged with hydrogen. No ammonia was formed when the nitrogen was first heated in a red-hot tube, or when it was obtained by passing atmospheric air over red-hot copper. From this Johnson concludes that nitrogen, like phosphorus, occurs in two modifications, only that formed in the cold being "active." These assertions were tested by Miss K. I. Williams and Ramsay,[2] but with a negative result. The total of "active nitrogen" found in 7·7031 litres of nitrogen prepared in the cold, as tested by the formation of NH_3, was only 0·000055 g.—that is, so slight a quantity that it must be attributed to accidental impurities not entirely removed by washing the gases. Johnson's statements have been also contradicted by Baker.[3]

Twinch (B. P. 3712, 1881) passes a mixture of steam, atmospheric air, oxide of nitrogen, and caustic-soda solution into a cylinder filled with granulated zinc. The oxide of nitrogen takes up the oxygen of the air, whose nitrogen then forms ammonia.

Brunel and Woog (*Comptes rend.*, 1907, cxlv., 922; *Chem. Centr.*, 1908, i., 209) employ nickel oxide as a catalytical substance for forming NH_3 from air and hydrogen at a temperature of 240° to 240° C., kept up by a boiling petroleum bath.

Ammonia can, by the action of catalyzers, at high temperatures be formed directly by the union of nitrogen and hydrogen. On the other hand, the same agency also decompose NH_3 into N_2 and H_2, so that we must write the equation:

$$N_2 + 3H_2 \rightleftarrows 2NH_3,$$

[1] *Chem. News*, xliii., pp. 42 and 288.
[2] *J. Chem. Soc.*, 1886. Proceed, p. 223.
[3] *Chem. News*, lxviii., p. 187.

and an equilibrium must exist between these two inverse reactions for every given set of conditions. On this point several communications have been recently made by Nernst, Haber with van Oordt and with Rossignol, and Jost, to which we cannot refer in detail (*Z. anorg. Chem.*, xliii., p. 111; xliv., p. 341; *Chem. Centr.*, 1905, ii., pp. 495 and 1300; *Z. Elektrochem.*, xiii., p. 521; xiv., pp. 181, 373, 509; *Ber.*, 1907, p. 2146).

The technical formation of ammonia by the direct union of nitrogen and hydrogen has been the object of several inventions which we now quote at some detail, although none of them appear to be sufficiently economical for practical purposes.

Woltereck (Ger. P. 146712; B. Ps. 2461 of 1902; 16504, 1904; 8358, 1905; F. Ps. 332591 and 345399; U.S. Ps. 803652 and 803653) prepares ammonia synthetically from mixtures of hydrogen and atmospheric air by means of intermediary substances acting as oxygen carriers, such as the oxides of iron, chromium, and bismuth. The ordinary contact substances, as platinum in a finely divided form,[1] charcoal, etc. (*cf.*, however, below!) cannot be applied here, since the oxide, reduced by hydrogen, must be always oxidized again in the presence of steam. The metallic oxides are, therefore, mere chemical agents, being reduced at the first stage and reformed at the second stage. He operates as follows. A mixture of atmospheric air and of gases containing free hydrogen, *e.g.*, ordinary coal-gas, more or less saturated with aqueous vapour, is passed over ferric oxide heated to a dull-red heat, preferably in the shape of rolls of iron wire, previously converted to ferric oxide. When employing ordinary coal-gas for this mixture, there is a strong formation of organic amines which must be decomposed by washing the product with strong alkaline solutions at a boiling heat and thus forming ammonia before the gases are absorbed by acid in the usual manner. Or else a mixture of about equal parts of atmospheric air and water-gas is more or less saturated with steam and treated in the same manner by passing it over the metallic oxide at a dull-red heat. In a laboratory experiment quoted by the inventor he obtained a

[1] Therefore the process, described in Ger. P. 74275, for producing ammonium bicarbonate or formiate by passing a mixture of CO or CO_2 with N, H, and steam over contact substances cannot be successful, since oxygen is absent here, as Woltereck found on putting it to a practical test.

yield of 6·3 per cent. of the theoretically possible quantity of NH_3, when employing coal-gas as the source of hydrogen.

Woltereck (*Comptes rend.*, 1908, vol. cxlvi., p. 194; *J. Soc. Chem. Ind.*, 1908, pp. 158 and 978; *Chem. Centr.*, 1908, vol. i., p. 1142) discusses his above-quoted proposals. When passing a mixture of air and hydrogen through water at 80 C., and then over reduced iron or the oxides of bismuth, chromium, and iron at 300° to 350° C., considerable quantities of NH_3 were formed. The result is very much improved by the introduction of steam. The best results are obtained by passing a mixture of 1 part H and 78 parts air, saturated with steam at 80 C., over iron-wire gauze, first oxidized, and before the experiment again reduced by means of CO, at a temperature of 300° to 350°. Thus from 100 litres air in 4½ hours 204 mg. NH_3 were obtained. Since the iron must be again brought to the metallic state before each experiment, Woltereck now states that it is better replaced by coke or charcoal. Eighty grams coke on burning by 868 litres air, saturated with steam at 80°, furnished in 47 hours at 400°, 337 mg. NH_3. Four hundred and forty-one grammes peat, treated in the same way, yielded even 11 g. NH_3 (8·25 g. of this being due to the peat itself, and 2·25 g. being synthetically produced from the atmospheric nitrogen). Small quantities of NH_3 were also formed when employing sugar-charcoal, free from N, at temperatures not above 700°. His British patent for this process is No. 28964, 1906. [In a polemical discussion, carried on in the "Technische Rundschau" of the *Berliner Tageblatt*, especially in No. 20, of May 19, 1909, Prof. A. Frank and Dr N. Caro distinctly deny any fixation of atmospheric nitrogen in the processes of Woltereck, against whose patents they have taken proceedings for cancelling them.]

L. Roth (Ger. P. 191914, of 1905) passes air through a porous medium into a mixture of 200 parts by weight of clay, 100 fine sand, 75 lime, 20 magnesia, 200 iron, and 600 water, heated to 60°. The specifically lighter nitrogen diffuses first through the medium and is retained in the form of NH_3, before the oxygen can act. When 10 mg. NH_3 has been formed for 1 litre of water, the formation of fresh NH_3 takes place much more slowly. But if now 1 per cent. ferric sulphate or ½ per cent. sulphuric acid is added, the mass again energetically forms

NH_3. Thus after a few hours a cheap fertilizer is obtained, containing 6 per cent. N, which is dried, ground, and used without extracting the ammonia.

In a later patent (Ger. P. 197393, of 1908) the same inventor, in order to prevent the injurious effect of the oxygen in the preparation of nitrides from air, separates oxygen and nitrogen by dialyzing the air by means of a finely powdered mixture of amorphous silicium carbide (obtained as a waste product in the manufacture of carborundum) with half its weight of iron, placed on slabs of burnt clay, 2½ ins. thick, built in a furnace. When forcing the air upwards through this mixture, the nitrogen passes through first and can be converted into nitrides.

The processes of Ireland and Sugden, who facilitate the formation of ammonia from atmospheric nitrogen by the interaction of *peat*, are described later on under that heading (Section H).

The aid of *electricity* for uniting nitrogen and hydrogen is invoked by many inventors. Thus Young (B. P. 1700, of 1880) passes electric sparks through a mixture of 3 vols. H + 1 vol. N (in this place we speak only of the direct union of H and N; the cases where intermediary compounds, nitrides, are in question, will be treated hereafter).

W. Müller and E. Geisenberger (Ger. P. 11489) employ combustion gases, which are freed from carbon dioxide by means of lime, as a source of nitrogen. Hydrogen is to be obtained by the action of steam on red-hot coke. The mixed gases are to be united by the electric spark. Another proposal of the same inventors (Ger. P. 12364) is: passing the gases, obtained by heating alkaline nitrates, along with steam, over red-hot coal. The alkaline residue is to be reconverted into the original salts by the joint action of oxygen, nitrogen, and the electric current.

The Société l'Azote (Ger. P. 17070) aims at combining the nitrogen of air with the hydrogen of water by the action of porous substances and of electricity. Melted zinc is run into two furnaces kept at a red-heat; into one of them is passed air, and water into the other. In both cases zinc oxide is formed; and there is liberated nitrogen on one side, hydrogen on the other. The gases are passed through dust-chambers to

deposit zinc oxide, and thence through retorts containing titaniferous iron-sponge. Here the nitrogen is first absorbed, and is then converted into ammonia by hydrogen. The formation of ammonia is promoted by employing in the retorts a mixture of iron with other metals, whereby an electric current is said to be produced (!). They also employ platinized coal, into which is forced first nitrogen, then hydrogen, at a pressure of ten atmospheres.

Nithack (Ger. P. 95532) produces ammonia by saturating water under high pressure with gaseous nitrogen, passing an electric current through this and continuing to introduce nitrogen under the same pressure. He asserts that the nitrogen is quantitatively transformed into ammonia, and that solutions of commercial strength are quickly formed. At the positive pole ammonium nitrate is formed. His process is carried out as shown in Fig. 213. The cylinder G contains at the bottom, sieves, S, for dividing the gas; at the top the non-conducting electrical portion, E. A number of carbon rods, K, connected by the metallic conductors *m*, form the hydrogen pole, a platinum wire-gauze cylinder, *p*, the oxygen pole; they are separated by the porous diaphragm *d*, tightly fitting on the annular bottom, *a*, of part E. Just below the level of the liquid, *d* is connected with a porcelain vessel, *i*, reaching to the top of G and preventing any mixture of oxygen and hydrogen. The apparatus D indicates any difference of pressure between the two chambers thus formed and remedies this at the same time. The ammonia liquor runs off through the perforated pipe a_1; the liquid formed at the oxygen pole passes through pipe a_2. *c* serves for introducing nitrogen, *b* for increasing the pressure, *v* for communication between the two electrode chambers; R is the washer, connected with the air-pump supplying the nitrogen.

After G has been filled with water, first low-pressure air, freed in the washer R from oxygen (?) and CO_2, is passed through T *r f* or T *c* a_1 into G, the water running off through F and valve v_1 to the level of the sieves S. Now v_1, *b*, and *c* are closed, and by means of a high-pressure pump nitrogen is forced in through R T *r* and *f* at 50 to 100 atmospheres' pressure, at the same time as water runs through pump P_1. As soon as the liquid has risen to *u*, the pole wires e_1 and e_2

are connected with the source of electricity. At K the nascent hydrogen forms with the nitrogen ammonia, which dissolves in the water and is carried off through a_1. At p at first only oxygen is formed and let out at D. Later on ammonia diffuses through diaphragm d and is oxidized to ammonium nitrate; if sufficient ammonia does not diffuse to fix all the oxygen, more is pumped in through n by means of pump P_2.

Briner and Mettler (*Comptes rend.*, 1907, cxliv., 694), when sparking a mixture of N and H at ordinary temperatures, produced only 3 to 4 per cent. NH_3, but at the temperature of liquid air almost complete combination was effected. The maximum

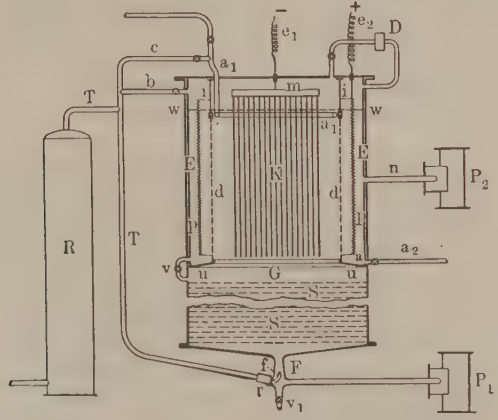


FIG. 213.

production occurred at a pressure of about 100 mm., when 0·17 g. NH_3 was produced per kilowatt hour.

The West Deutsche Thomasphosphatwerke (Ger. Ps. 157287 and 179300) make NH_3 from a mixture of hydrogen, nitrogen, and carbon monoxide by the dark electric discharge, carrying off the heat of reaction (which reduces the yield in consequence of the formation of ammonium formiate) by cooling arrangements, so that the temperature never exceeds 80° C., and is preferably kept at 65° C. In this case about 20 per cent. of the nitrogen can be converted into ammonia. The above mixture is most cheaply obtained in the shape of "mixed gas," by blowing air and steam into a gas-producer fed with coke.

Goriainoff (Fr. P. 368585) electrolyzes water, employing part of the hydrogen formed to prepare pure nitrogen from air by taking out the oxygen, and combining this nitrogen with another part of the hydrogen to form ammonia by means of electric discharges, or else with the electrolytic oxygen to form nitric acid.

Hooper (U.S. P. 791194) employs the electric current in this way: the cathode cell is filled with a solution of ammonium sulphate, the anode cell with a solution of sodium chlorides; the temperature is kept at 100° C. At the cathode NH_3 and H escape, at the anode Cl. This is united with the H to HCl, after taking the NH_3 out of the gaseous mixture.

Cassel (Ger. P. 175480) gets NH_3 by electrolysis of nitrates or nitrates, with addition of a small quantity of a soluble lead salt. The nitrates or nitrates are obtained from atmospheric air by the electric current.

2. *Synthesis of Ammonia by means of Nitrides.*

Several inventors aim at utilizing the intervention of the *boron nitride* for forming ammonia. Thus N. Basset (B. P. 4338, 1879) heats coal impregnated with boric acid, and covered with a layer of magnesia, lime, oxide of manganese, etc., in a retort, and passes nitrogen over the mixture. When a sufficient quantity of boron nitride has been formed, steam is introduced, and the ammonia now obtained is carried away.

G. N. Tucker (Ger. P. 13392) mixes carbon, impregnated with borates, with alkaline carbonates, or the oxides of manganese, antimony, iron, titaniferous iron, or with the borates of these metals. These are exposed to a red-heat in retorts; gas rich in nitrogen is passed in, so that the nitrogen combines with boron; then steam is passed in, which is decomposed by the carbon or the metal, and supplies the hydrogen necessary to form ammonia, Or else air or nitrogen and steam are mixed before introducing into the retort, in the proportion of 3 vols. H_2O to 1 vol. N. The borates and the metallic oxides contained in the residue are to be used over again. The gas is purified by milk of lime from carbonic acid, hydrogen, sulphide, and tarry substances.

Lyons & Broadwell (U.S. P. 816928, of 1906) pass nitrogen or gases containing such into a bath consisting of fused borates

of the positive metals, kept at about 1000° C. At the cathode, boron nitride is formed, which is afterwards transformed, by means of steam, at a temperature of 600° or upwards, into boric acid and ammonia:

$$2BN + 3H_2O = B_2O_3 + 2NH_3.$$

Mond (*loc. cit.*, p. 815) believes that boron nitride cannot be utilized for the purpose in question, owing to the high temperature required for its formation and the volatility of boric acid with steam. More success seems likely to be obtainable by Tessié du Motay's plan of preparing *titanium nitride*, and allowing a mixture of nitrogen and hydrogen tc act upon this. Titanium forms two nitrides, the higher of which is at high temperatures reduced by hydrogen to the lower, with formation of ammonia. When passing a mixture of hydrogen and nitrogen over the higher titanium nitride, Mond never obtained so much ammonia as would be formed without any free nitrogen. Hence the lower nitride does not combine with more nitrogen, which makes the process impossible.

Huntington [1] obtained from titanium nitride, prepared from titanium and nitrogen, only traces of ammonia by means of hydrogen.

Hlavati [2] prepares a contact substance from layers of titanium, nickel, titanic iron, platinum black, or indifferent porous substances on which titanium or platinum has been superficially precipitated. He burns hydrogen or hydrocarbons in air, and passes the products of combustion through the above substance at a high temperature, or else he passes electric currents through.

Wilson (B. P. 21755, 1895) prepares *magnesium nitride* from magnesia and carbon in the electric furnace in a current of nitrogen, and decomposes this by steam into ammonia, magnesia being regenerated. The nitrogen is obtained from atmospheric air, depriving this of oxygen by red-hot coke to transform it into CO, or preferably blowing the furnace for CO_2, and fixing this by lime, so as to obtain pure N. Compare the criticism of this patent in *Z. Elektrochem.*, 1896, p. 274.

Rossel and Franck (*Chem. Zeit.*, 1896, 38) equally obtain NH_3 from magnesium nitride, preparing this in a most im-

[1] *Eng. and Min. J.*, 1892, p. 607. [2] *Chem. Zeit.*, 1895, p. 2214.

practicable and costly way by heating calcium carbide and metallic magnesium in the presence of air.

Mehner (B. P. 12471, 1895; B. P. 2654, 1897; and B. P. 28667, 1903) again prepares nitrides by the electric furnace, in order to transform them into oxides and ammonia.

Kaiser (B. P. 26803, 1905; Ger. P. 181657; Fr. P. 350966) obtains NH_3 by heating *calcium nitride* in a current of hydrogen under high pressure; the calcium is reduced to the metallic state, or to a hydride when the hydrogen is in excess. If now nitrogen is passed over it, calcium nitride is re-formed. A continuous production of NH_3 can be effected by heating metallic calcium alternately in a current of nitrogen and hydrogen. This takes place all the more readily when the metal is deposited on asbestos in a finely divided state. The reaction sets in at about 150° C.; the best results are obtained between 200° to 400°.

Borchers and Beck (Ger. P. 196323, of 1908) prepare nitrides of metals from atmospheric nitrogen by the assistance of the electric current in a similar way, as in the electrolysis of alkaline chlorides, where the cathodic mercury is charged with alkaline metal, which is taken out of it, so that the mercury can be used over again. An alloy of *tin and magnesium*, electrolytically formed, is by the action of nitrogen in another space partially converted into magnesium nitride; the alloy, now containing much less Mg, returns to the cathode space to be again enriched with Mg. The magnesium nitride is converted into ammonia by means of water or of steam, and the process may be conducted in such manner that anhydrous ammonia and anhydrous MgO are formed. The latter is used over again in the electrolytic cell.

Another patent for that purpose is that of Roth (Ger. P. 197393).

Cerium nitride is employed for the synthesis of NH_3 by Lipski (*Z. Elektrochem.*, 1909, p. 189), *Aluminium nitride* by Bronnert (*Bull. Soc. Ind. Mulhouse*, 1909, p. 39).

3. *Ammonia from Atmospheric Nitrogen by the Intervention of Cyanides or Carbides.*

The fact that nitrogen combines with carbon and alkalis at a high temperature has been known for a long time. According

to Breneman,[1] Dawes in 1835 drew attention to the presence of potassium cyanide in blast-furnaces. After the hot blast had been introduced, the formation of saline masses was observed containing upwards of 40 per cent. potassium cyanide, with some carbonate. In 1839 Lewis Thompson[2] obtained potassium cyanide by heating coke, potashes, and iron filings in the presence of air to a bright red-heat. Fownes and Young[3] repeated his experiments. Most celebrated were the researches of Bunsen and Playfair,[4] who removed every doubt concerning the formation of cyanides in blast-furnaces, and at the same time proposed a method for utilizing this reaction for the actual manufacture of potassium cyanide. In fact a small works was erected near Paris by Possoz and Boissière to work this process, which was subsequently transferred to Newcastle-on-Tyne, but this had to be given up after great losses. Later on Bramwell made some improvements in the process, but his factory, also near Newcastle-on-Tyne, was likewise stopped after losing a large amount of money. This lack of success was due to the extreme temperature required causing a large consumption of fuel, much loss of potash by volatilization, and extensive repairs to the apparatus.

Newton (B. P. 9985, 1843) proposed using the gases from vitriol-chambers for the above process, after purifying them by ferrous sulphate.

The first who utilized this process for the manufacture of ammonia was Swindells (B. P., 12th June 1844) by mixing steam with the nitrogen acting on red-hot coke. Further patents were taken by Binks, Armengaud, and Ertel (*Dingl. polyt. J.*, cxx., pp. 77 and 111).

In 1860[5] Margueritte and Sourdeval found that caustic baryta is much more active towards nitrogen than potash, because it is neither fusible nor volatile: the former quality prevents the external fusion of the mass, whereby the action of the gases on the interior is impeded; the latter prevents loss by volatilization—both very awkward drawbacks in the case of potash. Still, the manufacture of cyanides or ferrocyanides by

[1] *J. Amer. Chem. Soc.*, xi., Nos. 1 and 2; *Z. angew. Chem.*, 1890, p. 173.
[2] *Dingl. polyt. J.*, lxxiii., p. 281. [3] *J. prakt. Chem.*, xxvi., p. 407.
[4] *Rep. Brit. Assoc.*, 1845.
[5] *Comptes rend.*, vol. l., p. 1100; B. P. 1027, 1860.

the baryta process would seem to be too difficult; but Margueritte and Sourdeval at once aimed at forming the cyanide only as an intermediate product, and utilizing it for the formation of ammonia by the action of steam, thus:—

$$Ba(NC)_2 + 4H_2O = 2NH_3 + Ba(OH)_2 + 2CO.$$

They made a mixture of native barium carbonate with coal-tar, pitch, and sawdust, with or without iron filings, which was strongly ignited in a fireclay retort till the barium carbonate had been converted into a porous mass of barium oxide. Through this they passed at the proper temperature a slow current of air, the oxygen of which had been previously converted into carbon monoxide by red-hot coal: thus barium cyanide was formed. This was cooled down to 300°, and steam was passed through. All the nitrogen of the cyanide is evolved as ammonia, and the barium hydrate remaining behind can be used over again.

This process did not pay, owing to technical difficulties, and seems to have been neglected. Moerman-Laubuhr, in 1875, took out a French patent[1] for the following process:—

Bricks are made of pulverized charcoal or coke and alkaline carbonates, and are exposed in a small blast-furnace to the action of air, previously deprived of oxygen by red-hot coal; the cyanide collects in the melted state at the bottom, and is tapped off from time to time; whereupon it is converted into ammonia by various methods, unnecessary to describe here, as the process evidently turned out a complete failure.

Margueritte and Sourdeval's process was taken up again by L. Mond (B. P. 433, 1882), who carried it out in the following form. The barium carbonate is powdered and incorporated with small coke from pitch or oil residues, charcoal, pitch, tar, paraffin residues, and so forth. In lieu of barium carbonate it is possible to employ a solution of its oxide or salts, or of alkaline oxides or salts; for instance, the solution obtained by lixiviating the used briquettes. The most advantageous proportions are:—Thirty-two parts barium carbonate, 8 parts charcoal or coke, and 11 parts pitch. The addition of alkalis is not of much use. This mixture is formed into briquettes, which it is necessary to heat in a reducing flame till the pitch is coked, and the barium carbonate converted partially or

[1] No. 108037; *Bull. Soc. Chim.*, vol. xxvi., p. 46.

completely into oxide. The briquettes may be broken up into small lumps, and such lumps may also be formed by heating the mixture of barium carbonate or carbon on the hearth of a reverberatory furnace or in a revolving furnace by means of a reducing flame until the mass is fritted, when it is discharged and broken up into lumps.

These lumps or briquettes are charged into kilns arranged in the same way as an annular kiln, so that some of the chambers are being heated while others are cooling down or are being filled or emptied. A gaseous mixture, as rich as possible in nitrogen, and containing little carbonic acid, oxygen, and aqueous vapour, heated to a temperature of about 1400° C., is passed into the chambers filled with briquettes, until a sufficient quantity of cyanogen compounds has been formed. When this is the case, the stream of heated gas is shut off, and cold gas of the same or similar composition conducted into the mass until the temperature has fallen to 500° C. If the aim be to produce ammonia, the stream of gas is now suspended and the material treated with steam; ammonia hereby results, is aspirated off and absorbed or condensed. If, however, the aim be to produce cyanogen compounds, the mixture in the chamber must be cooled to at least 300° C. At this temperature it may then be safely removed, lixiviated with water, and the cyanogen compounds obtained from the solution in the usual manner. In order to obtain ammonia, the mass is treated with steam or a fine spray of water at a temperature of 300° to 500°. The lumps thus dealt with may repeatedly undergo the same treatment, until most of the carbon is consumed. As sources of nitrogen, the gases evolved from the carbonic-acid absorption-apparatus of the ammonia-soda process, and the gaseous mixture obtained by the combustion of coal or coke with the smallest possible quantity of hot air, are the most profitable; and the requisite temperature is most readily obtained by means of a Siemens recuperator, applying this also to the previous heating of the air employed for the combustion. The gases leaving the last chamber which is being heated at the time must be further cooled down by passing them under a boiler or pan, or through a washing-apparatus, before they get into the chamber where the material is just cooling. After having fulfilled this object, these gases, which contain much carbon

monoxide, may be burned and used as a source of heat; for instance, for heating air, generating steam, and for other purposes.

For work upon a moderate scale, the following process and plant are recommended. In a heating-chamber, B (Figs. 214 and 215), four earthenware retorts (A) are arranged in couples. Into this combustion-chamber, heating-gas and air, previously heated in a recuperator, enter by the slits *c*, the products of combustion being forced by the wall *a* to surround the retorts and thoroughly circulate before passing to the recuperator R. The lower divisions (H) of the retorts (A) are made of iron, and are either surrounded by water or are kept constantly sprayed by means of the jets *e*. The tubes D serve to introduce the gases rich in nitrogen into the cooling-chambers H, and by the tubes *d* the passage of steam is effected. The retorts A having been charged with the briquettes, the temperature is raised to 1100° to 1400° C., and nitrogen passed in through D, traversing the mass in H and abstracting heat therefrom. From time to time *n* is closed and portions of the product are removed by the door S, new briquettes being fed in at N. For the conversion of the resulting cyanogen compounds the masses taken out of H at a temperature of 300° may be treated in a separate apparatus; or, more simply, the cock *n* is closed, and through the subjacent mass, still at a temperature of 500°, steam is passed by means of the tube *d*, the ammonia formed issuing at *m*. When the formation of ammonia has ceased, the portion of the retort below the cock *n* is emptied; the cock is opened in order to fill that space again, and a fresh charge of briquettes is introduced at the top of A. In some cases it will be found advantageous to use hot generator-gas instead of a cold gaseous mixture containing nitrogen. Requiring less heat from B, the work done by the retorts will be thereby increased, but the cooling-space H will require to be enlarged, since it is only cooled from without. But the cooling within the space H may also be hastened by passing in cold gases at D, and at the same time hot generator-gases at *v*. In the latter case an opening must be provided in the upper part of H just below *v*, by which the greater part of the cooling gases may escape; and it is best to provide a cock or slide between these two parts. The gases which leave the retorts A, being rich in carbon monoxide, may be utilized for heating purposes.

Mond's process, although tried on a somewhat large scale, did not come into practical operation. The process requires a very large amount of heat to be communicated through the

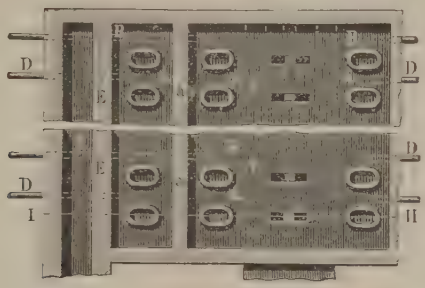


FIG. 214.

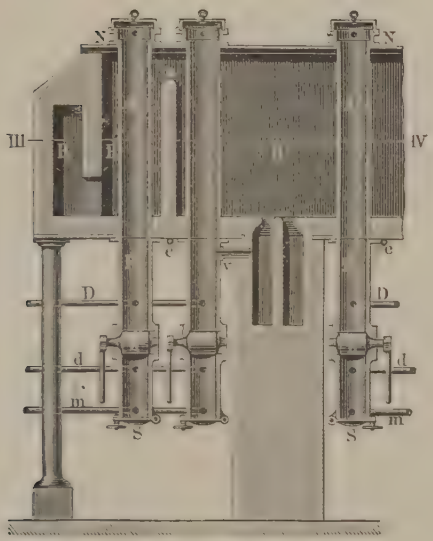


FIG. 215.

earthenware sides of a retort, which wastes too much fuel, even if retorts similar to those of zinc-works are employed. This cannot pay whilst so many other sources of ammonia are available.

Another development of the same method has been attempted by L. Q. Brin and A. Brin (B. P. 3089, 1883), combining with it the manufacture of barium peroxide, according to their patent No. 1416 of 1880 (Ger. P. 15298). There are two sets of retorts. One of them contains barium oxide, which is kept at a temperature of 600°, and retains the oxygen of the air passed in, with formation of barium peroxide. The remaining pure nitrogen is pumped over into the second set of retorts, charged with "barytic coke," at a temperature of 800°. The barytic coke is made from equal parts of barium oxide or carbonate and charcoal powder, agglomerated by coal-tar. Thus the barium is completely transformed into cyanide, which is converted into NH_3, CO_2, and BaO by passing in steam at a temperature of 300°. The second set of retorts is heated with generator-gas, and the surplus heat of the fire-gases serves for heating the first set of retorts.

Blairs (*Dingl. polyt. J.*, ccxxx., p. 93) employs a cupola filled with a mixture of carbon and potash, heated from the outside.

J. Young (B. P. 16046, of 1885) recommends as a suitable material for retorts, destined for manufacturing cyanogen compounds by the above described processes, non-acid and non-metallic substances. Compressed coke or plumbago answers moderately well; but magnesian limestone is the best. The raw limestone is calcined, ground, mixed with tar, moulded and reburned, exactly as is done for bricks used in the Thomas-Gilchrist dephosphorizing process. [It is more than doubtful whether such retorts would stand the wear and tear of the process, and a "basic" material does not seem to be called for in this case, as the baryta mixture does not fuse.]

Another modification of the above principle is that patented by T. B. Fogarty (B. P. 5361, 1883). He leads ordinary producer-gas, freed from moisture and in a high state of incandescence, downwards through a tower in which a shower of intimately mixed and finely comminuted carbon and alkali is constantly falling. At the bottom of the tower is a pit containing water to catch the falling material, provided with an opening for the escape of the gas. A great deal of the nitrogen of the producer-gas is taken up by the carbon and alkali to form alkaline cyanides, which are met in their downward course by a steam-jet introduced into the lower part of the tower.

Thus the cyanogen compounds are decomposed, ammonia being formed, which is then washed out by scrubbers. The gas left after this treatment is next conducted into a retort where ordinary bituminous coal mixed with alkali is undergoing distillation. Here a further combination of nitrogen with carbon and alkali takes place, with formation of cyanogen compounds. Some of these are decomposed by the aqueous vapour in the retorts, but the bulk remains in the coal left behind in the retorts. The producer-gas here serves as a diluent or absorbent of the rich hydrocarbon vapours which are given off by the coal in the early stage of the distillation, and which would otherwise be converted into tar. After leaving the retorts, the gases are again scrubbed for ammonia. When the distillation is finished, the coke is brought, with as little exposure to the air as possible, into a closed vessel, where a stream of water is allowed to play upon it from the top. The steam thus generated decomposes the cyanides with evolution of ammonia, which passes upwards through the new cool layers of coke above, and with the gases generated simultaneously is led away and recovered by scrubbing.

Later on (B. P. 13746, 1887; U.S. Ps. 417778, 1889, and 615266, 1899), Fogarty modified his process. He passes a mixture of air and steam through red-hot carbon, and thereupon through a white-hot retort, filled with powdered carbon and alkali. A feeding-worm constantly introduces alkalized carbon at the top, which lower down meets with nitrogen and steam. The cyanides formed are at once decomposed into NH_3, CO_2, CO, and K_2CO_3. A hydraulic main keeps back the fixed particles mechanically carried along, after which the gases pass through condensers and scrubbers.

De Lambilly (B. P. 16049, 1890) mixes equal volumes of air (freed from oxygen by red-hot copper) and coal-gas (freed from all hydrogen and most hydrocarbons by the cupric oxide formed as above). The mixture is freed by caustic lime from carbon dioxide and steam, and is slowly passed over a mixture of sodium, potassium, or barium carbonate with coke and lime (previously heated till no more CO is evolved) at a white heat and at a plus-pressure of 10 or 15 cm. quicksilver. The gases have thus time to form cyanides, and only H and CO escape, which are utilized for heating the furnaces. The process can be

improved by mixing with oxides, granular iron, nickel, or cobalt. The cyanides formed are mixed with the theoretically necessary quantity of water, and after 24 or 48 hours the ammonia obtained by the reaction

$$CNK + 2H_2O = HCOOK + NH_3$$

is expelled by heating in retorts.

Quite similar are the processes of J. Young (B. P. 24856, 1893), Mackay & Hutcheson (B. Ps. 6925 and 13315, 1894), J. C. Fell (B. P. 20722, 1889), and others.

Readman (B. P. 6621, 1894) heats a mixture of 1 part carbon and 5 parts barium carbonate with air in an electric furnace. Willson (B. P. 21997, 1895) passes nitrogen into calcium carbide, to produce the reaction $CaC_2 + N_2 = Ca(CN)_2$, whereupon ammonia is formed by the action of superheated steam. Mehner (Ger. P. 92810) employs an electric furnace, into which carbon and alkali are introduced from the top, together with air. The gases and cyanide vapours are taken away quite hot and carried into a cooler, filled with coal or coke, where they condense and are treated with steam.

We mention further the German patents of Gilmour (No. 73816), Alder (Nos. 12351, 18915, 27334), Nithack (No. 95532), Caro & Frank (Nos. 88363, 92587); also the American patent of Dankworth (No. 569325).

Breneman[1] states the following conditions as most suitable for the formation of cyanogen from C and N:—A bright red-heat; absence of oxygen, but little water (more for ammonia); most intimate mixture of all reagents; the presence of a strong base (even ammonia may serve in some cases), preferably potash, or else baryta among alkaline earths. Probably ammonia and cyanogen are formed at different temperatures and degrees of moisture. CO and other reducing gases seem to answer the purpose; O, CO_2, and excess of steam are certainly injurious. SO_2 and H_2S are hardly suitable. Hydrocarbons are favourable, and sometimes dispense with the presence of a base. The influence of pressure is as yet unknown.

In a similar way Fawsitt[2] discusses the conditions of the

[1] *J. Amer. Chem. Soc.*, xi., Nos. 1 and 2; *Z. angew. Chem.*, 1890, p. 173.
[2] *J. Soc. Chem. Ind.*, 1890, p. 30.

process. Hempel[1] declares pressure to be useful for promoting the formation of cyanogen.

A new line of departure in this field was taken by Professor Frank and Dr Nikodem Caro, who act on the principle that *carbide* of sodium, calcium, baryum, etc., is formed in the first instance, and these are only subsequently transformed into cyanides by the influence of nitrogen under special circumstances. Berthelot (*Comptes rend.*, lxvii., p. 141) had already assumed this to be the case, and had also shown that under the influence of the electric arc acetylene combines with nitrogen to form potassium cyanide. Caro (*Chem. Ind.*, 1895, p. 287) declared this reaction to be possible of execution on the large scale, and Figuier (*Comptes rend.*, cii., p. 694) thought of combining nitrogen and methane. But nothing has come of this, while the intermediary formation of carbides has been developed by Frank and Caro, to an extraordinary extent. On this Caro has reported at length in a lecture reprinted in *Z. angew. Chem.*, 1906, pp. 1569 *et seq.*; and Frank, in *J. Soc. Chem. Ind.*, 1908, pp. 1093 *et seq.*

The following is a list of the patents of Frank and Caro, mostly taken out in their own names, but partly in that of the Cyanid-Gesellschaft, Berlin, which has taken them over, and in that of patent agents:—

Ger. P. 88363 of 1895, preparation of cyanides from carbides.
„ 92587 of 1895 (the same—addition to the former).
„ 95660 of 1896 „
B. P. 15066 of 1895 (the same).
Fr. P. 249539 of 1895 „
Ger. P. 108971 of 1898, preparation of cyanamide salts.
„ 116087 of 1898 „ cyanides.
„ 116088 of 1898 „ „
Fr. P. 289828 of 1898 „ nitrogen compounds.
B. P. 25475 of 1898 „ „
Ger. P. 134289 of 1900 „ ammonia from cyanamides.
„ 152260 of 1901, artificial nitrogenous fertilizers.
„ 157503 of 1902 „
Fr. P. 319897 of 1902 „
B. P. 15976 of 1902 „
„ 17507 of 1902 „

[1] *Berl. Ber.*, 1890, p. 3388.

Ger. P. 150878 of 1902, calcium cyanamide (Stomps).
Fr. P. 328031 of 1902 „
B. P. 16298 of 1902 „
Fr. P. 382743 of 1907, nitrogen compounds from carbides; and two additions.
B. P. 5314 of 1907 „ (Bloxam).
Ger. P. 203308 of 1907, nitrogen compounds of alkaline earths from carbides.
„ 204882 of 1907, pure nitrogen from combustion gases.

We now give a short outline of their principal results, going into more details upon their later patents. Calcium (or barium) carbide is treated at red-heat with atmospheric nitrogen, *e.g.*, such as is obtained by passing air through red-hot copper, contained in outwardly heated retorts, which fixes the oxygen and allows the nitrogen to escape. Of course the nitrogen may be obtained by any other means, *e.g.*, the Linde process, consisting in the fractional distillation of liquid air. This nitrogen is passed through a retort, containing the carbide; as the reaction is exothermic, the retort requires only at first heating from the outside; later on, the process of fixing the nitrogen goes on by itself, until all the carbide has been consumed. The reaction consists in the formation of calcium (or barium) cyanamide and cyanide. Possibly the latter is formed in the first instance:—

$$CaC_2 + N_2 = CaC_2N_2,$$

and is later on converted into cyanamide:—

$$CaC_2N_2 + N = CaCN_2 + CN.$$

When working with calcium carbide, at the proper temperature, only traces of cyanide are left. The product obtained, consisting essentially of cyanamide, mixed with carbon (graphite), has been called "Kalkstickstoff" (lime nitrogen); it contains 20 to 24 per cent. nitrogen, and may be used directly as a fertilizer, in competition with nitre or ammonium sulphate. But it may also be employed for the production of ammonia, by being spread on trays and subjected to the action of superheated steam:—

$$CaCN_2 + 3H_2O = CaCO_3 + 2NH_3.$$

The graphite formed during the production of "lime nitrogen" can be separated cheaply and in a very pure form,

by a process worked out by Frank, Caro, and Jacoby, and they state that the cost of converting the nitrogen into "lime nitrogen" is entirely covered by the value of this graphite. Caro further reports on the application of lime nitrogen to the manufacture of potassium cyanide, as well as to the conversion of iron into steel and to other purposes into which we cannot enter in this place.

The Frank and Caro inventions are worked on a large scale by Messrs Siemens & Halske and by a special company, formed for that purpose, and called the "Cyanid-Gesellschaft." In the year 1908, already £5,000,000 had been invested in that affair in Europe and America. Most of the factories, some of which will produce 40,000 tons of lime-nitrogen per annum, were still in course of erection when these lines were written, but some were already fully at work.

A French patent (No. 382743, of 1907) has been obtained by the Cyanid-Gesellschaft for the manufacture of nitrogen compounds by means of carbides. When the carbide of a metal belonging to the group of alkalis or alkaline earths, is treated in a current of nitrogen at one point, the reaction will propagate itself throughout the mass, if the necessary initial temperature is reached. The preliminary heating may be brought about electrically, or by passing heated nitrogen over the carbide, which itself may be heated moderately, or by the addition of another constituent to the nitrogen or the carbide (*e.g.*, oxygen or aluminium powder), which shall, by reaction with some substance present, liberate the necessary heat.

The Ger. P. 203308 of the Cyanid-Gesellschaft, Berlin, attains the same purpose by adding salts of cyanamide to the carbide, *e.g.* calcium cyanamide. This avoids the addition of alkaline oxides, carbonates, dioxides, fluorides, etc., and produces an article of high percentage, and well adapted for manurial purposes.

To this patent additions have been made, dated 11th and 12th October 1907:—(1) The nitrogen is made to pass over the mass in a direction opposite to that in which the reaction is being propagated. This prevents local fusion. To avoid an aggregation of the particles, indifferent substances, such as carbon, wood, crude calcium cyanamide, etc., may be added. (2) For the purpose of starting the reaction by means of electrical heating,

vertical cavities are constructed in the mass, formed of some conducting material which is destroyed as the temperature rises and the cohesion of the mass increases. The electro-heaters are thus introduced without coming into actual contact with the material. The carbide is surrounded by a layer of some porous substance, not affected by nitrogen, *e.g.* sand, which protects the walls of the containing-vessel and ensures a more uniform distribution of the gas.

The B. P. 21786, of 1906, by A. R. Frank and M. Voigt, incorporates the same invention.

A German patent of Frank and Caro, No. 204882, of 22nd May 1907, describes a process for preparing pure nitrogen from combustion gases, by passing them over a mixture of a metallic oxide and free metal. Producer-gas is burned by secondary air, the products of combustion are cooled and purified, and then passed through a retort charged with a mixture of metallic copper and cupric oxide. Here the oxygen is retained by the metal's carbon monoxide, and the hydrocarbons are burned by the mediation of the cupric oxide, and the resulting CO_2 is separated from the nitrogen by absorbents.

The *Chem. Zeit.*, 1907, p. 527, contains a glowing report on the development of the industry of calcium cyanamide. Its efficiency for agricultural purposes is stated to be quite on a par with that of nitrates. The problem of utilizing the nitrogen of air may be taken as resolved now, and at an early future this will be the only source of nitrogen compounds for fertilizers.[1] The Società generale della Cianamide at Rome is the owner of the patents in that line, also those of Frank and Caro. Special limited companies have been established in Germany, England, Italy, Austria, France, and Switzerland, for exploiting them. The factories already at work or in course of erection are: Bromberg, in Germany (2500 tons cyanamide per annum); Oddo, in Norway (12,500 tons); Piano d'Orto, in Italy (10,000 tons); Dalmatia (10,000 tons); Notre Dame de Briançon, in Savoy (3750 tons); Martigny, in Switzerland (3750 tons).

According to a report in the *Z. angew. Chem.*, 1909, p. 1040, several of these establishments are working very success-

[1] This is an overstatement of the case! According to Wagner and other authorities, the manurial value of "lime-nitrogen" is only four-fifths of that of "nitric nitrogen."

fully, and are largely increasing their plant, especially those working with water-power in Italy, France, North America, and Canada.

The whole question is very ably summed up in a pamphlet by Dr Nikodem Caro — *Die Stickstofffrage in Deutschland* (The Nitrogen Question in Germany)—published in 1908, and by his paper read at the International Chemists' Congress in London in 1909. A study of the fixation of nitrogen by calcium carbide has been made by Pollacci (*Z. Elektrochem.*, 1908, p. 565). He finds that potassium carbonate exerts a catalytic action on the absorption of nitrogen by calcium carbide, lowering the temperature required. The best results are obtained with an addition of 4 per cent., and by working at a pressure of 2 atmospheres, at 900° to 950°, when after one hour 23·0 per cent. of N was found to be converted into calcium carbide.

Similar processes have been developed on other sides, to which we now turn.

Cunnington (B. P. 25605, 1906) prepares nitrogen from air, especially for the cyanamide process, as follows. He burns limestone and coke in a lime-kiln from which a mixture of CO_2 and N, with very little O, passes away. These gases are passed through an ammoniacal solution of common salt, whereby the CO_2 is removed, and practically pure N is produced. The $NaHCO_3$ formed in this process is utilized in the usual way.

Hoyermann (*Chem. Zeit.*, xxvi., 70) reports on his attempts of converting atmospheric nitrogen into ammonia.

Lance and Elworthy (B. P. 4409, 1906; Fr. P., 355504) again prescribe the manufacture of ammonium cyanide, and afterwards of other nitrogenous compounds, by passing a mixture of methane, nitrogen, and hydrogen over heated pumice or metallic nickel.

Borchers and Beck (Ger. P. 196323) describe an electrolytic process for the preparation of nitrides from metallic oxides or salts by means of atmospheric nitrogen.

A French patent of the Gesellschaft für Stickstoffdünger, No. 375979; and a British patent, No. 9407, of 1907, of the same, together with C. Krauss; also a German patent, No. 198706, of 1907, prescribes accelerating the decomposition of cyanides and cyanamides by the addition of calcium chloride. Powdered calcium cyanamide is mixed with an equal weight of a con-

centrated solution of $CaCl_2$. The paste solidifies on standing; it is then broken into pieces and heated in a retort, the ammonia evolved being collected. Towards the end of the reaction a little steam may be injected, in order to prevent a decomposition of ammonia in contact with the hot sides of the retort.

Serpeck (Ger. P. 181991, 1905; Fr. P. 367124) exposes *aluminium carbide* in the state of powder preferably mixed with coal to the action of atmospheric nitrogen at higher temperatures, such as can be obtained in a crucible heated by a blast-fire. Within a few minutes the reaction is complete, and a hard, bluish mass is formed, which smells of NH_3 in damp air, and yields up all the N taken up from the air as NH_3.

According to his German patent, No. 183702, 1905, he now prefers mixing the aluminium carbide with alumina or alumina compounds and coal, heating with access of air or nitrogen until a *partial* formation of aluminium carbide has taken place, reducing the product to powder, and only then exposing it to the action of nitrogen at higher temperatures.

That powerful concern, the Badische Anilin- und Sodafabrik of Ludwigshafen, has also done a large amount of labour in this field, as shown by the following patents.

In order to prepare ammonia from the cyanides of the alkaline-earth metals, the Badische Anilin- und Sodafabrik (U.S. P. 914468, taken by Bosch; Fr. P. 372714), instead of treating it, as formerly usual, with water at temperatures between 300° and 500° C. (which leads to the formation of CO and H), heats the crude cyanides (400 kg., coarsely ground) with water (600 litres) in high-pressure apparatus slowly up to 150° C., until the saponification is complete. The NH_3 is then let off, together with steam, and the perfectly pure gas is treated in the usual manner. The yield is nearly quantitative, and from the residue *formic* acid can be recovered in almost the theoretical quantity. (The English patent for this process is taken out in the name of J. V. Johnson, B. P. 22038, 1906.)

The Badische Anilin- und Sodafabrik (Fr. P. 387001) also prepares cyanides and cyanamides from titanium cyanonitride by melting it with calcined sodium carbonate and lampblack, or by heating it with quicklime, calcium chloride,

and lampblack. The titanium may afterwards be readily reconverted into the nitride or cyanonitride. Their Fr. P. 387002 shows that the nitrogen present in these titanium compounds may be readily converted into ammonia by most of the oxidizing agents, or by heating with acids in the presence of water or steam. The titanic acid formed in this process, when heated with carbon and salts of alkaline metals, absorbs nitrogen at a comparatively low temperature. Thus a mixture of 80 kg. titanic acid, 20 kg. wood-charcoal, and 2 kg. sodium sulphate requires heating in a current of nitrogen for 2 hours at about 1240° C.

The Ger. P. 200988 of the same firm treats of the preparation of cyanides and cyanamides of the alkalis and alkaline earths by heating the nitrogen compounds of titanium (the nitride and the carbon-nitrogen compound) with the oxides, carbonates, or other salts of the alkalis or alkaline earths in the presence of carbon, pitch of the like, with or without a flux. The titanic acid formed in this process can be reconverted into the nitride or carbon-nitrogen compound in the well-known manner.

The Ger. P. 202563 of the same firm, dated 10th March 1907, produces ammonia from the cyanogen-nitrogen compound of titanium by heating this with oxidizing agents (apart from caustic alkali) at a suitable temperature, in neutral, alkaline, or acid solutions, suspensions, or in the state of fusion. Such agents are, *e.g.*, sulphuric acid and sodium bisulphate, together with water under pressure; or electrolysis, with or without oxygen carriers; or air, with water, with or without the assistance of high pressure and of oxygen carriers.

The Ger. P. 203748 of the same firm (to which corresponds the B.P. No. 1842, of 1908, taken out by Johnson for the B.A.S.-F.) describes a modification the process of Ger. P. 202563. The titanium cyanonitride is soaked with a contact substance, *e.g.*, a solution of platinum chloride, and is then heated to 300° to 400° in a current of air and steam. Their Ger. P. 203750 describes the heating of titanic acid with coal in a current of nitrogen, after adding an alkaline salt (sulphate or carbonate), which enables the reaction to take quickly and at comparatively low temperature. The alkaline salts seem to play the part of nitrogen carriers, since already small quantities produce a

strikingly hastening action). Their Ger. P. 204204 protects the application of titanium nitride, Ti_2N_2, in lieu of the cyanonitride. Their Ger. P. 204475 shows that in this process steam may be employed as an oxidizing agent, if at the same time such metallic salts, oxides, or hydroxides are present which under the circumstances of the case do not themselves oxidize the titanium nitrides. Their Ger. P. 204847 describes the preparation of ammonia from titanium nitride by boiling this with sulphuric acid of 30 per cent., with exclusion of air. When employing concentrated sulphuric acid, the temperature must be kept below 170° C., to avoid the oxidizing action of the acid. The corresponding British patents, taken out by J. V. Johnson, are Nos. 2414 and 2525, of 1908.

Scientific laboratory investigations on the fixation of nitrogen by the carbides of alkaline metals have been made on various sides; thus, by Moissan (*Comptes rend.*, 1894, pp. 503 and 685); Bredig (*Z. Elektrochem.*, 1907, lxix., 605); Förster and Jacoby (*ibid.*, p. 101); Rudolfi (*Z. anorg. Chem.*, 1907, 170); Kühling and Berkold (*Ber.*, 1908, 28; *Z. angew. Chem.*, 1909, 193); Lipski (*Z. Elektrochem.*, 1909, p. 189).

We here give a short abstract of the results.

Calcium or barium carbide in the *pure* state are very little acted upon by nitrogen; up to 1200° C., they fix little or nothing of it. But the impure technical products do so at very much lower temperatures, so that some of the foreign substances present (chlorides, oxides of various metals, etc.) must exercise a sort of contact action, which is distinctly evident from Frank and Caro's technical results (*supra*). Barium chloride alone seems to influence neither the temperature at which the reaction begins nor the total amount of nitrogen fixed, but it seems to favour the formation of cyanide at the expense of cyanamide. But the *oxides* have a very strong action, although it is not yet known which of them are most efficient. They cause the absorption of nitrogen to begin already at 500° or 600° C., and the amount fixed at higher temperatures to be much greater than otherwise, the maximum being reached at 920° to 930° C. If barium chloride, say, 10 to 30 per cent. of it, is present at the same time as the oxides, etc., the rate of absorption increases further till the temperature of 1120° to 1130° is reached, and the yield is also decidedly increased thereby.

Up to the time of closing this chapter there was still very much wanted to elucidate this subject.

C. Ammonia formed in various Anorganic Chemical Processes.

In some cases where nitrate of soda is used for oxidizing purposes, ammonia is formed, and proposals have been made for its utilization. This is, for instance, the case with the ammonia formed in very perceptible quantities during the oxidation of the sulphur compounds in the manufacture of caustic soda.[1] It would seem very difficult to recover this slight quantity of ammonia dispersed in an enormous volume of other gases. But at the Aussig Chemical Works this is actually done; and, in 1884, 60 tons of ammonium sulphate were obtained from this source.

In "black-ash" obtained by the Leblanc process there is always a certain amount of cyanides, which cause a good deal of trouble in the manufacture of pure soda. Matthieson and Hawliczek have worked out a process[2] by which they transform the cyanide into ammonia by means of superheated steam at 300° to 500°. An account of this is given in the author's *Sulphuric Acid and Alkali*, 2nd edition, vol. ii., p. 574.

Even less advantage can be expected for the process of Görlich and Wichmann (Ger. P. 87135), who allow the H_2S, evolved in the Leblanc process or otherwise, to act upon sodium nitrite:

$$NaNO_2 + 3H_2S = NaOH + 3S + NH_3 + H_2O.$$

Tralls (Ger. P. 41352) recovers ammonia in the manufacture of sulphate of alumina from bituminous schist by adding a little gypsum before calcining the schist.

Bondouin and Escarpit[3] manufacture ammonia by heating 100 sodium nitrate with 40 naphthalene to 600° in a continuously fed retort. Quite similar to this is Fouler's process (Ger. Ps. 57254, 75610, 76724).—It is hardly to be expected that much ammonia will be formed by this reaction.

Kellner (Br. P. 13722, 1893) electrolyzes sodium nitrate in

[1] *Cf.* especially Lunge and Smith, *J. Soc. Chem. Ind.*, 1833, pp. 460 and 525.

[2] B. P. 5456, of 1886; *J. Soc. Chem. Ind.*, 1889, p. 351.

[3] Fr. P. 205584; *Chem. Zeit.*, 1891, p. 184.

the following way:—A solution of sodium is electrolyzed with a mercury cathode, and the sodium amalgam formed is employed as cathode in a solution of sodium nitrate, into which dips a second electrode, in order to recover the electric current generated during the action of the Na on $NaNO_3$, in which NH_3 and NaOH are formed.

Raschen and Brock (B. Ps. 7287 and 7288, 1895) treat equal molecules of sodium nitrate and chloride with an excess of sulphuric acid; the nitrosyl-chloride formed is mixed with hydrogen and is passed over hot platinum-asbestos, the reaction being:

$$NOCl + 6H = NH_4Cl + H_2O.$$

If NOCl is replaced by N or oxides of nitrogen, free NH_3 is formed.

The West Deutsche Thomasphosphatwerke (Ger. P. 157287) subject a mixture of hydrogen, nitric oxide, and carbon monoxide to the action of spongy platinum, at a temperature not exceeding 80 C. and aided by the silent electric discharge. In practise the mixture would be made of Dowson gas or water-gas and nitric oxide. A mixture of 12 vols. H., 40 NO, 44 CO, and 4 CO_2 yields on the average about 10 vols. NH_3.

Cassal (Fr. P. 346066) absorbs the gases produced by the action of an electric discharge on air, and consequently containing nitrogen oxides, in caustic alkali so as to form nitrates and nitrites, and electrolyzes the solution without a diaphragm. Ammonia is liberated as a gas, and the caustic alkali is reformed. The yield is improved by addition of 5 per cent. of lead nitrate. Nitrites must be present, unless a small-current density is used at the cathode. Instead of caustic alkali, lime or calcium carbonate may be used as the absorbent.

Angelucci (*J. Soc. Chem. Ind.*, 1907, p. 147, from *Gazz. chim. ital.*, 1906, p. 517) obtained ammonium carbonate from acetylene and nitric oxide by passing them through spongy platinum heated to 800° C.

Görlich and Wichmann (Ger. P. 87135) prepare ammonia by decomposing alkaline nitrites with sulphuretted hydrogen.

D. Ammonia from Urine, Sewage, etc.

Urine is no doubt the oldest source of ammoniacal compounds, and up to a comparatively recent period it was practi-

cally the only one for manufacturing purposes. The oldest chemist who really deserved that name, the Arabian Geber, who lived in the eighth century, undoubtedly prepared sal-ammoniac from urine and common salt. Sal-ammoniac, made in this way, was an article of commerce in Europe as early as 1410; and the Jesuit Sicard in 1720 describes a manufactory of it in the Delta of the Nile which he had visited. In Egypt sal-ammoniac was made by mixing camel's dung with salt, burning it, and collecting the sublimate; we shall give some more particulars concerning this subject in the section "Sal-ammoniac" in Chapter XIV.

Putrefied urine (in which the urea has passed over into ammonium carbonate) has been used for centuries, and to a certain extent is still used by dyers as a source of ammonia for scouring wool and other purposes.

The methodical collection of urine or sewage and working it up into ammoniacal compounds has been carried out in the neighbourhood of some large towns, *e.g.*, Paris; but this industry represents only a very small proportion of the enormous quantity of animal ejections passing off in other ways, and it furnishes only a comparatively small fraction of the ammoniacal compounds required in trade. If all the ammonia corresponding to London urine were recovered, this would amount to the enormous total of more than 60,000 tons of sulphate per annum.

Normal urine contains from 20 to 35 g. urea per litre: an adult man produces from 22 to 37 g. urea per 24 hours, along with $\frac{1}{30}$ to $\frac{1}{60}$ of that weight of uric acid; this corresponds to 12·5 to 21 g. NH_3 per day, or between 9 and 17 lb. per annum. Urine, left to itself, after a short time begins to ferment, the result being that urea, or carbamide, $CO(HN_2)_2$, takes up $2H_2O$ and is changed into ammonium carbonate, $(NH_4)_2CO_3$, under the influence of a microscopic fungus.

In Paris[1] there are daily 2200 cbm. (say, tons) of urine and night-soil taken out of the "fosses," partly disinfected by sulphate of iron or zinc, and are left to settle in large reservoirs, where the solid matters separate from the liquid sewage, forming 85 to 95 per cent., which is now called "eau

[1] C. Vincent, "Industrie de Produits ammoniacaux," *Enc. Chim. Frémy*, 2nd edition, 10th vol., 4th part, p. 7.

vanne." In 3 or 4 weeks the fermentation is complete, the urea has vanished, and there is formed principally ammonium carbonate, along with sulphhydrate, sulphate, chloride, ammonio-magnesian phosphate, compound ammonias, and other substances of intensely disagreeable smell. There is always a considerable loss of nitrogen, partly as such, partly by the evaporation of ammonia, and partly by its oxidation into nitric acid. When the fermentation is complete the clear "eau vanne" is drawn off from the muddy deposit, which is converted into manure, but always with much loss and causing a great nuisance.

Several processes have been introduced for treating this very disagreeable deposit, of which we will give an outline. The Bilange process, practised at Bondy, is applied to the whole of the sewage. This is mixed by mechanical agitators with an exactly measured quantity of chemicals, intended to promote a rapid settling, principally consisting of milk-of-lime of specific gravity 1·16 to 1·20. The mixture is allowed to settle in tanks, holding 500 tons each. After an hour the clear liquid is pumped away; it has an amber colour and contains free ammonia. The albuminoid matters are precipitated along with carbonate of lime and most impurities. The decanted liquid is replaced by a fresh mixture from the agitators; the clear portion is again decanted, and this is continued until the tank is full of deposit. The thick mud is now heated by steam (it is more easily pressed in this state) and is passed through filter-presses. The ammonia escaping during the heating is retained in tanks filled with sulphuric acid. The cakes turned out from the filter-press are much richer in nitrogen the less lime has been used. Each 100 cbm. of crude sewage yield 75 cbm. clear decanted liquid and 25 cbm. deposited mud, from which is obtained 6 or 7 tons of cakes containing 50 per cent. moisture. The manurial value of the latter is very small. The liquid is worked up in the ammonia-stills.

The Kuentz process has been worked in several places, *e.g.*, at Versailles. The crude sewage is received in closed tanks, where it passes through zigzag channels, and thus undergoes a first settling. The clear liquid issuing at last is sent to the ammonia-stills. The thick deposit is pumped into a closed mixer, where it receives an addition of the chlorides of aluminium and iron and of phosphate of lime, in order to make it pass through the

filter-press and enhance its manurial value. The reagent is prepared by treating a mixture of 15 parts bauxite, 75 parts natural phosphate of lime, and 3 parts hydrated oxide of iron (yellow hematite) with 110 commercial hydrochloric acid and 150 water. Fifty kilog. (1 cwt.) of the liquid resulting from the reaction is added to each cubic metre of thick mud. After 24 hours' settling a considerable quantity of clear liquid, with only a faint smell, collects at the top and is decanted, and the deposit is forced by compressed air into a filter-press. The cakes contain all the phosphoric acid as bicalcic phosphate, precipitated by the ammonium carbonate, along with calcium carbonate; the iron has absorbed the sulphur compounds, and the alumina has modified the albuminous and slimy matters which otherwise would have impeded the filtration. The percentage of nitrogen in these cakes is 3 to 3·5, that of assimilable phosphoric acid 10 to 12 per cent.

The ammonia-stills must be specially adapted to avoid the smell inherent to such matters; they will be described in the last chapter.

It is hardly necessary to observe that all such processes apply only to concentrated night-soil, not to sewage diluted with a large quantity of water from water-closets, etc.

Ketjen[1] reports on a successful experiment, made at Amsterdam, for recovering most of the nitrogen of sewage by distillation with lime. The apparatus was similar to that employed in distilling gas-liquor, sufficient to work up 50 tons in 24 hours. The sewage contained 2·018 per cent. free and 0·326 "fixed" ammonia; only 0·00848 per cent. NH_3 remained in the waste-liquor. 8750 tons of sewage yielded 72 tons sulphate of ammonia, with the expenditure of 123 tons quicklime, 153 tons coal, and 72 tons sulphuric acid, sp. gr. 1·7. The fixed residue, mixed with lime and pressed in a filter-press, contained 58 per cent. dry substance, 52·27 per cent. $CaCO_3$, 0·518 per cent. N, 0·155 per cent. K_2O, and 0·157 per cent. P_2O_5. Neglecting its manurial value (which for some soils is not *nil*), the profit made on the sulphate of ammonia reduced the expense of dealing with the sewage to 44 cents. (say 9d.) per ton of sewage, so that it was resolved to erect a plant for 250 tons per diem, in order to deal with the whole Amsterdam sewage.

[1] *Z. angew. Chem.*, 1891, p. 294.

We will now enumerate various patents referring to this subject.

J. P. Rickman and J. B. Thompson (B. P. 3305, 1882) add to urine and night-soil putrefying ox-gall as a ferment. The upper space of the closed tank in which the mass is kept is connected with a reservoir containing sulphuric acid, to absorb the ammonia escaping. The liquid remaining in the fermenting-tank is afterwards distilled at a low temperature; the vapours from the directly heated still first pass through liquid contained in a cold still and thence into the absorbing-vessels.

J. Young (B. P. 3562, 1882; Ger. P. 27034) distils off a portion of the sewage, or of the effluent waters of sugar manufactories, either by itself or mixed with lime, at a pressure above or at or below that of the atmosphere; the distillate contains a greater proportion of ammonia than the original sewage. His apparatus consists of a series of long boxes, arranged like steps, and provided with false bottoms inclined in such a way that when the boxes are filled with the liquid, which is previously warmed and mixed with lime, the steam which is admitted at the bottom can be sucked by means of a vacuum backwards and forwards through the whole battery of boxes, while fresh liquid flows continuously in at the top and out at the bottom. Instead of the boxes, cylinders may also be employed.

J. Duncan (Ger. Ps. 27148 and 28436) treats sewage, mixed with lime and cleared by settling, with steam in such a manner that the boiling-point 30 C. is never exceeded. This is done by means of a series of vessels combined into a battery, in which the liquid travels in the opposite way to the steam. When the liquid contains only about 0·5 g. NH_3 per litre, steam takes up hardly more than $\frac{1}{800}$ of its weight of NH_3 in a vacuum in which water boils at 21° C. It is therefore best to take the ammonia out of the steam by sulphuric acid, and employ the "purified" steam over again (?).

F. J. Bolton and J. A. Wanklyn (Ger. P. 17386) pass the vapours from heated sewage, etc., mixed with air or carbonic acid, through layers of porous calcium sulphate, mixed or not with calcium and iron phosphate, of calcium chloride, of its double salts with potassium or sodium chloride, or of potassium-magnesium chloride. The ammonium carbonate is transformed with those reagents into calcium carbonate and ammonium

sulphate or chloride. When the reaction has gone far enough the mixture is heated, whereupon the inverse reaction takes place; ammonium carbonate escapes [of course in a dissociated form], and the original salts remain to be used over again.

C. H. Schneider (Ger. Ps. 27671 and 32890) promotes the natural settling of sewage by the addition of calcium chloride, whereby the ammonia is converted into a non-volatilizing compound; the slimy matters are also precipitated, and with old sewage a clear liquid is obtained which is easily decanted. With fresh sewage a further clarification by aluminium sulphate is advisable.

Richters and Hagen (Ger. P. 14210) force air into the mixture of sewage or night-soil with lime, by means of perforated pipes, and condense the ammonia in coke-scrubbers by sulphuric acid.

Brullé and Leclerc (B. P. 1086, 1880) run the sewage, etc., in thin layers over heated surfaces, and cause a current of air, passed over those surfaces, to carry away the ammonia.

I. van Ruymbecke (U.S. P. 342237, of 1886) seeks to submit liquids containing organic substances to a rapid putrefying process, by allowing them to act in the shape of a spray on substances impregnated with putrefaction-ferments in the presence of a strong current of air, so that air, ferment, and liquid are brought into intimate contact. The escaping air is deprived of its ammonia by treatment with sulphuric acid, and the residual liquid is also treated for ammonia as usual.

Buhl and Keller (Ger. P. 27671) precipitate the phosphates with lime salts and crude manganese chloride (still-liquors from the manufacture of chlorine); the settled liquor is distilled for ammonia. In lieu of manganese chloride, aluminium or zinc sulphate may be employed, say, from 4 to 16 kg. zinc sulphate to a ton of sewage, according to its consistency. This causes a kind of curdling, by which the liquids can be easily separated from the solids. The latter are filter-pressed and dried, yielding 1 to 1½ cwt. per ton of sewage, with 2·6 to 3·5 per cent. N. and 5·5 to 6·3 per cent. phosphate of lime. The filtered liquid is distilled with lime, and yields 75 per cent. of the NH_3 present in the sewage.

Wedemeyer's process for recovering NH_3 from sewage (Ger.

P. 87591) and Bruch's process (Ger. P. 79486) can be only mentioned here.

On boiling fibrous matters (for paper or pasteboard) with lime at 8 atmospheres' pressure, about half of the N. present is given off as NH_3. But according to Nast (Ger. P. 40980) all the nitrogen is transformed into NH_3, if besides 5 per cent. lime, 2 per cent. NaCl is added (?).

Schilling and Kremer (B. Ps. 15752, 1903; 14966, 1904; Aus. P. 20602) allow the sewage to stand for some time in coke or slag filters, let it run off, and pass hot gases, especially those produced in burning the mud collected on the gravel filters, through the empty filters, taking the gases to ammonia absorbers and thus obtaining the NH_3 retained by the filters, as well as destroying the substances which stop up the filters.

Fryklind (B. P. 20241, 1904) mixes sewage, stable manure, etc., with quicklime; the heat generated thereby expels the ammonia, which is absorbed in a suitable way.

The Gesellschaft für Abwasserklärung, Berlin (Ger. P. 161166) separates the muddy deposits from the clear sewage and burns it, passing the gases through the clear portion of the sewage during the filtration, and from these by means of a fan-blast into an absorber for ammonia.

Twynam, Egham, and Matthews (B. P. 2625, 1895) filter the sewage through a mixture of ferric hydroxide and phosphates, or a hydrated phosphoric iron ore, and afterwards expel the absorbed NH_3 by steam, or use the mixture directly as a fertilizer.

Naylor (B. P. 17650, 1902) mixes the refuse with lime and passes it through a chamber into which air, heated by the hot flue gases leaving the destructor furnace, is forced. The NH_3 is condensed as usual.

Butterfield and Watson (B. P. 19502, 1905) distil the pressed sewage sludge by means of heat and steam in vertical retorts with continuous action by means of the heat produced by the waste gases.

J. Jean & Cie. (Fr. P. 372171) pass the sewage on to a quickly rotating fan, thus producing a dense mist, which is passed through baffle-plates on which the water condenses; the air is then brought into contact with an acid to retain the ammonia.

Taylor and Walker (U.S. P. 603668) employ a vertical retort, with injection of steam under the grate.

Matthiessen (Ger. P. 89147) passes volatile organic compounds of any sort over a red-hot contact substance consisting of an alkaline or earthy aluminate.

Fryklind (U.S. P. 918744) distils the excrements with lime into sulphuric acid, contained in a closed vessel, and utilizes the steam produced in the latter for the primary distillation.

E. Ammonia from Guano.

Apart from the deposits of ammonium bicarbonate sometimes found in Peruvian guano (p. 814), it is possible to extract considerable quantities of ammonia from guano by heating it with lime. This process was patented by Young in 1841; but it cannot be remunerative, since the direct manurial value of guano is superior to that of the ammonia salts obtainable therefrom. This is best proved by the proposal of Bunte and Grahn (Ger. P. 47601) to increase the ammonia present in guano or superphosphates by passing the ammonia obtained from gas-liquor directly into superphosphate. For 20,000 cbm. gas 1 cbm. superphosphate, with 18 or 19 per cent. soluble phosphoric acid, is employed. The superphosphate is thus used twice over, until 7 or 8 per cent. N are accumulated in it. According to Ries[1] this process has done excellent service at the Munich gas-works.

F. Ammonia from Bones, Horn, Leather, Wool, Hair, and other Animal Substances.

The carbonization of *bones* is employed on a large scale for the manufacture of bone-charcoal, a substance very largely used in sugar manufactories and for several other purposes. In Germany and France this is generally done by heating the bones in iron pots, one on top of another, which are placed in large numbers in a furnace, heated by a fireplace built on one side of it. Thus the gases proceeding from the fireplace become mixed with those escaping from the carbonizing bones, and the ammonia contained in the latter is too dilute to be condensed; but there is also too little of it to begin with, as the temperature

[1] *Fischer's Jahresber.*, 1888, p. 91.

in this case is very high and most of the ammonia is destroyed.

In England and Scotland bone-charcoal is generally made by heating the bones in iron or fireclay retorts, provided with condensing-apparatus similar to that of gas-works. In these a kind of tar, called "Dippel's oil," and some ammoniacal liquor are collected. This tar consists to a great extent of pyridine derivatives, and is partly worked for these. The ammoniacal liquor is worked up exactly like that of the ordinary gas-works; it is probably more contaminated than the latter with pyridine bases.

The proportion of ammonia formed in this case is much larger than when charring the bones in pots, as in the former process the gases are subjected to cooling immediately after leaving the retorts, while in the latter they are exposed to the full heat of the fire-gases, and the ammonia is thus decomposed. Moreover, the temperature attained in the retorts is lower than that in the pots, which is precisely the reason why many continental manufacturers prefer the latter system, as the bone-char is of better quality.

The bones intended to be charred must be first freed from fleshy particles, etc., by steeping in water (preferably tepid) for 24 hours, and mechanical cleaning; they are then roughly broken up by fluted rollers and are submitted to the process of removing the grease. This formerly always consisted in boiling them in water, preferably in a butt or pan, heated by a steam-coil, in which the bones were suspended in wire-work baskets; after a few hours' boiling, all the grease was found floating on the top and was carefully ladled off, after which the baskets holding the bones were lifted out, the bones then thoroughly washed, and at last dried by prolonged exposure to the air. Several processes have been introduced for removing the grease by washing with bisulphide of carbon, benzoline, and the like, in specially constructed closed apparatus, which admit of recovering the solvent, but which cannot be described here.

The dried bones are sometimes at once admitted to the charring process, especially when this takes place in retorts; but where they are to be charred in pots, the bones are usually first broken up by studded or fluted rollers, and the pieces sorted by machinery, so that the different sizes required by the consumers of bone-char are obtained beforehand. The smaller

particles, which are of very little value as char, are ground up into bone-dust for manure, the larger pieces are separately charred.

The retorts for charring bones are sometimes horizontal, of a section similar to gas-retorts, and are fired in the same way; sometimes they are, however, perpendicular, in which case they can be worked continuously, part of the contents being from time to time withdrawn at the bottom, and cooled without contact with air, while fresh bones are being introduced at the top. The gases are conveyed away by a lateral tube near the top, and are first passed through a hydraulic main, or some similar apparatus, where they have first to traverse a shallow layer of water; they then pass through a cooling-apparatus, which may consist of a series of upright metal pipes, connected alternately at top and bottom, and cooled by air or by a water-spray, and afterwards through an ordinary scrubber. The remaining gases, which still possess a very disagreeable smell, are conveyed back into the retort-fire and are there burnt. Care must be taken to introduce them in a very hot place, so that the combustion may be complete. Of course it is preferable to promote the passage of the gases by an injector or exhauster.

The condensing liquids are allowed to settle in tanks where the tar (Dippel's oil) is separated; it amounts to 1·7 to 2 per cent. of the weight of the bones, and unless it is worked for pyridine, etc., it is mostly burned as fuel under the retorts. The ammoniacal liquor is worked up like gas-liquor, as will be shown in the 14th Chapter; it generally yields from 6 to 7 per cent. of ammonium sulphate of the weight of the bones, of somewhat inferior quality and strongly coloured. (If all the nitrogen contained in the bones were converted into ammonia, this would amount to 20 or 25 per cent. of sulphate.)

A process sometimes followed in France consists in filtering the crude ammoniacal liquor through a layer of plaster of Paris (sulphate of lime); the ammonium carbonate is thus transformed into sulphate, which is recovered by evaporation, insoluble carbonate of lime remaining on the filter.

H. P. Lorenzen (Ger. P. 9989) passes the gases evolved in charring bones over red-hot lime, where the tarry matters are burned, and condenses the ammonia in coke-scrubbers charged with dilute sulphuric acid.

H. J. and E. B. Castner (B. P. 4057, 1882) also carry the products of the continuous distillation of bones, along with air, through heated tubes, thence over hydrate of lime, and, after cooling, into sulphuric acid. [The addition of air and subsequent heating would tend to destroy much ammonia.]

A material similar to the tar from bones, etc., is the "*acid tar*" of the Scotch mineral-oil works. From this tar, which contains a considerable quantity of pyridine bases, Redwood[1] obtains ammonia by neutralizing the acid with lime and distilling with superheated steam, thus producing a neutral tar and 21 per cent. of the nitrogen present in the shape of NH_3.

Other animal refuse (wool, hair, skin, horns, feathers, sponges, leather, and so forth) is principally employed for two purposes, namely, for manufacturing prussiate of potash and for manure. In the former case the refuse matter is sometimes charged directly, or after being simply dried, into melted carbonate of potash, and in this instance of course no ammonia can be recovered. But sometimes the animal matters are first charred in retorts, exactly as has been described for charring bones, and the ammonia formed is recovered in the same way. It has been found that the charred matters yield the same quantity of cyanogen compounds as if they had been employed in the raw state, that is at most one-fifth of the quantity corresponding to their percentage of nitrogen (say 10 to 15 per cent.). Hence all the ammonia recovered in the charring process would seem to be a clear gain; but in spite of this not much is made in that way, as the expense of charring in retorts in any case swallows up most of the profit. One thousand parts of horn on carbonizing furnishes, according to Dumas, 500 parts of ammoniacal liquor at 8° to 10° Tw. and 160 parts of Dippel's oil. Some of the ammonia can be obtained as a solid sublimate of crude ammonium carbonate.

The utilization of these refuse animal matters for manurial purposes is effected in different ways. Sometimes they are exposed to the action of steam in closed cylinders, when they become friable and are then ground up and mixed with superphosphate, etc. Sometimes they are added without any preparation to manures otherwise prepared, but in this case they

[1] *J. Soc. Chem. Ind.*, 1891, p. 108.

disintegrate in the soil with extreme slowness. The most successful treatment of these substances seems to be: dissolving them in hot concentrated sulphuric acid (which can be performed in cast-iron vessels), and utilizing that acid for manufacturing superphosphate. In this instance most, if not all, the nitrogen is converted into ammonia, as is done in Kjeldahl's analytical process for determining the percentage of nitrogen. But this ammonia is, of course, never separated in the free state or in the shape of a salt, being at once incorporated with the other parts forming the chemical manure.

Another process admits of recovering the ammonia as such, and is also, as it were, based upon an extremely well-known analytical process, namely, the estimation of nitrogen by soda-lime. L'Hôte treats the refuse matters with a 10-per-cent. solution of caustic soda, in the cold or at such a moderate temperature that no ammonia is set free. The substances are thus converted into a pulp or completely dissolved. This pulp or liquid is mixed with slaked lime and the solid mass is charged into cast-iron retorts, where it is heated at first only gently, to avoid a destruction of ammonia, afterwards to a red-heat. The ammonia contained in the escaping gases is condensed by means of sulphuric acid. The residue is composed of sodium carbonate and lime, and when treated with water regenerates the caustic soda [no doubt only imperfectly], which can be used over again.

H. Proschwitzky (Ger. P. 10957) charges retorts with alternate layers of 1 part of refuse leather and 4 parts of lime. The gases evolved by heating are first passed through condensing-apparatus for separating tar, ammoniacal liquor, and crude ammonium carbonate, and thence into sulphuric acid. The remaining mixture of charred leather and lime is to serve as a manure. The uncondensed gases are used for heating the retorts.

Th. Richters (Ger. P. 13594) soaks leather, blood, wool, hair, and other animal refuse with a solution of carbonate of potash, dries the mass, and heats it in retorts, without proceeding to fusion. The volatile products (ammonia, tar, and gas) are treated in the usual manner. The residue contains potassium cyanide, cyanate, sulphocyanide, carbonate, hydrate, sulphide, and carbon. It is lixiviated with water in the presence of metallic iron or ferric hydroxide; thus the potassium cyanide is

converted into ferrocyanide (prussiate of potash), which is recovered by crystallization; the mother-liquor is used again for treating animal matters, and the caustic potash contained therein is converted into carbonate by admitting carbonic acid during the drying process. [An altogether similar process for the simultaneous manufacture of prussiate of potash and ammonia was tried as early as 1860-62, by myself, in company with another chemist, on a practical scale, and some tons of both products were manufactured; but the process was given up on account of the difficulty of preventing the mass from fusing in the retorts, which made its discharge a very awkward operation and rapidly destroyed the retorts. It is, however, possible that these technical difficulties might be overcome. The ammonia is, of course, quite a secondary product in this case, the value of the prussiate of potash being far greater.]

W. H. Marriott (B. P. 4369, 1881) distils animal refuse in a kiln by introducing at the bottom a mixture of producer-gas and the exact quantity of air necessary for burning it.

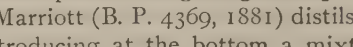
De Bonardi (B. P. 29009, 1896) passes city garbage through a continuously working incinerating-furnace.

The experiments made by Mond (*J. Soc. Chem. Ind.*, 1889, p. 505) for recovering ammonia from refuse leather, with or without lime, did not yield any satisfactory results.

From "Seeschlick," *i.e.*, deposits containing a great deal of organic matter and probably of marine origin, found in large quantities near Stettin, the Deutsche Ammoniakwerke recover ammonia by destructive distillation, preferably in the moist state (Ger. P. 115462). In Ger. P. 142505 they describe a furnace specially constructed for that purpose. According to Knublauch (Ger. P. 137453) the yield of ammonia is greatly improved if the "Seeschlick" is mixed with coal previous to the distillation.

G. Ammonia as a By-product in the Manufacture of Beetroot Sugar and of Alcohol.

Beetroot contains betaine (trimethyl-glycocol):



also asparagin: $CH_2(NH_2)—COOH$

$CH_2 . CO . NH_2$

and other chemical compounds, from which, by decomposing reactions, ammonia (along with trimethylamine) is split off. This is facilitated by the addition of lime to the beetroot juice, for the purpose of purifying it; and, in fact, the juice, after this treatment, during its concentration constantly emits small quantities of ammonia. It has been several times proposed to recover this ammonia. Thus, Vibrans (Ger. P. 15513) aspirates the steam and ammonia collecting in the upper part of the "thick juice" evaporators by means of a pump, and passes it through an acid; he also treats in a similar way the ammonia given off in the "saturating-pans." Hudec (*Fischer's Jahresber.*, 1895, p. 817) obtained from the condensed water of the evaporating-boilers 0·032 g. NH_3 per cubic metre. More can be got by spraying alum solution into the boilers, or, according to Pölecke (Ger. P. 52885), gaseous or sprayed acids.

It is, however, much more important to recover the ammonia found in a more concentrated state in the "*vinasse*," that is the residue from subjecting the molasses to fermentation, and distilling off the alcohol. The best-known process is that of Cam. Vincent,[1] which has for its principal object the manufacture of trimethylamine and methylic chloride, but considerable quantities of ammonia are likewise obtained (about 32 cwt. of ammonium sulphate from 98 tons of molasses, or 400 tons of vinasse, treated per diem). The evaporated vinasse is ignited in retorts and the gases submitted to condensation; the tarry liquid which separates is saturated by an acid and evaporated to a certain degree; on cooling, the ammonia salts, which are less soluble than the others, crystallize out. A further quantity of ammonia is obtained in the dry distillation of the trimethylamine hydrochlorate, in a similar way to the above. The ammonium salt thus obtained (generally the hydrochlorate) is much contaminated with the chlorides of iron and lead from the metal of the vessels; it is purified by dissolving in water, adding ammonium sulphide, filtering, crystallizing, and draining the crystals in a centrifugal machine.

E. Ernst (Ger. P. 13871) mixes with the vinasse, concentrated to 76° Tw. and still hot, 25 per cent. dried ground peat, 3 per cent. ground quicklime, and 6 per cent. fatty oil. The mixture is charged into a semicircular piece of sheet-iron, which

[1] *Comptes rend.*, 1877, 21 mai and 8 octobre.

is placed in a red-hot horizontal retort, iron rails preventing a direct contact between the sheet-iron and the retort-shell. The gases formed are treated as usual. Further patents of the same inventor (Ger. Ps. 17869 and 18549) describe other arrangements for igniting mixtures of vinasses with peat, etc.

R. Lederer and W. Gintl (Ger. P. 17874) calcine the concentrated vinasse in a continuous stream, at a temperature of 350 to 400° C., in a horizontal retort, fitted with an Archimedian screw, so that the char continuously issues at the other end, ready for the recovery of potash salts, the gases being treated by Vincent's process.

F. X. Brosche (Ger. P. 14433) believes that 60 or 70 per cent. of the nitrogen of the vinasse can be recovered as ammonia by dry distillation of the vinasse over potash-lime, formed by a mixture of carbonized vinasse with lime. Up to 80 per cent. is obtained if the vapours are, moreover, passed through a tube filled with potash-lime.

The Badische Gesellschaft für Zuckerfabrikation (Ger. P. 15702) extracts carbonized vinasse with water, causticizes the solution by lime, evaporates the liquor, and adds so much of it to concentrated vinasse that there is from 5 to 15 parts of potassium hydrate present for each 100 parts of dry vinasse. The dry distillation is then carried on as usual.

Haring, Ehrenberg, & Co., and M. Baswitz (Ger. P. 15751) introduce concentrated vinasse, or the liquors from the osmose and elutriation processes, in a very thin stream into retorts heated to a dark red-heat, so that there is almost instantaneous gasification. The gases, which are very rich in tarry matters, are subjected to overheating in pipes placed between the retorts, where the tar is destroyed [along with some of the ammonia?], and thence pass into the condensing-apparatus.

Even from the *potash* made from vinasse, which contains some potassium cyanide, Legrand and Dabernard (Fr. P., 27th Dec. 1876) believe that they can obtain ammonia by treating it with steam. Thus 1 to 4 per cent. ammonium sulphate is to be obtained from potash. [This will hardly pay!]

Emil Meyer (Ger. P. 43435) proposes working the liquor left on recovering sugar from molasses not merely for ammonia and alkali salts, but also for oxalic acid, by fusing the salts with

caustic soda or potash; C. Uhl & Co. (Ger. P. 47190) propose improvements to this process. Sternberg (Ger. Ps. 78442 and 105638) evaporates the same liquor with coke, and distils the mixture in retorts with superheated steam, which converts much more of the nitrogen into NH_3. The formation of ammonia commences at 100° C.; at 300° 50 per cent. of the nitrogen compounds are converted into NH_3, and at 500° the decomposition is practically complete. His apparatus is shown in Fig. 216. It consists of three superposed retorts, connected by vertical pipes and fitted with agitating-worms. a_1 is the charging-funnel, d the discharging-pipe. The fire-gases travel along A, B, C, D, E, F, and through G into the chimney. The

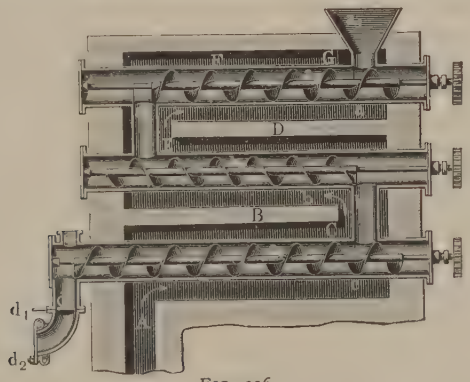


FIG. 216.

material enters at a_1 and proceeds along a, a_2, a_3, into b, then along b_1, b_2, through c, c_1, into the cooler d, and is discharged by d_1 and d_2. d can be connected by e with a gas-pump, which serves for aspirating air from a_1 right through the retorts.

H. & W. Pataky (Ger. P. 86400) mix the evaporated liquor with alumina and distil in retorts; the residue contains potassium aluminate, besides other salts.

Mathiessen (Ger. Ps. 89147 and 93397) also employs alumina in various forms for increasing the yield of ammonia from molasse-liquors.

Cf. also Schiller's process (Ger. P. 38596).

In treating molasses with lime and alcohol, for the purpose

of recovering the sugar, the alcohol distilled off from the calcium saccharate contains ammonia. H. Steffens (Ger. Ps. 23594 and 24549) treats it with sulphuric, carbonic, sulphurous, or phosphoric acid, or acid salts, in order to recover the ammonia.

Effront (Fr. P. 369630, and Ger. P. 209114, of 1909) increases the yield of NH_3 from boiled-down vinasse by mixing it with resins or with acid salts, obtaining part of the NH_3 by drying the mixture in a current of hot air and distilling the residue at 700° C. in presence of superheated steam and of an excess of air. Another patent of the same inventor (Fr. P. 382689) employs butyric-acid ferment at 38° to 42° C. During the fermenting process, which lasts about three days, 15 to 20 litres of butyric acid are formed. An alkalinity of about 1·5 g. per litre must be maintained by the addition of lime.

Ost (*Z. angew. Chem.*, xix., p. 609) describes the utilization of vinasse by the process used at the Dessau works.

Sternberg (B. P. 7002, of 1896; Ger. P. 105638) mixes the sugary liquor with a crude potassium aluminate, obtained from bauxite, and heats the blocks thus made in a continuously acting retort.

Fischer (B. P. 15815, of 1899) heats thickened vinasse in a series of retorts, provided with alternately working screws to from 200° to 500° C.

Besemfelder (Ger. P. 118795; U.S. P. 689780) mixes the concentrated waste lyes of sugar-works with bauxite, or alumina and coke, and heats the mixture in a series of horizontal superposed pipes. The gases are conveyed into "decomposition-retorts," and the tar produced there, together with ammonia, is separated therefrom.

Andrlik (*Chem. Zeit.*, 1902, rep. p. 274) describes his experiments with the same material, especially the use of certain bacteria for converting the nitrogen into ammonia.

Further patents in this line are: Peceker Zuckerraffinerie (Aus. P. 1284); Sudre and Thierry (Aus. Ps. 5158, 5159, 6861, 8878).

H. Ammonia from Peat.

Several of the processes for obtaining ammonia, described in the preceding sections, employ peat as an auxiliary, together with other materials. In this section we treat of the recovery of ammonia from peat where this is the principal substance.

The importance of utilizing peat more than has been done in the past, also in the direction of turning its nitrogen to account, follows from the vast surface of land covered by it. Prussia alone possesses about 5 million acres of peat land; the vast extent of this in Ireland is well known.

Peat contains a very considerable quantity of nitrogenous compounds, most of it probably already in the form of ammonium salts, partly formed by the decomposition of organic matter, and partly absorbed from the atmosphere. The nitrogen found in it sometimes amounts to 4 per cent., and by dry distillation the best descriptions of peat yield up to 8 per cent. by weight of ammonium sulphate; even inferior qualities yield about half that amount.

According to researches made by Chuard (*Comptes rend.*, cxiv., p. 181), the soil on the top of peat-bogs, which is distinctly acid, acts in a strongly nitrifying way, producing in 3 months 0·020 per cent., in 6 months 0·062 per cent., in 12 months 0·298 per cent. N_2O_5. Calcium carbonate here seems to have rather an injurious action. It is uncertain whether the nitrifying process in this case is identical with that going on in ordinary soils.

The dry distillation of peat further yields a tar very rich in phenols, acetic acid, and paraffin, and it has been worked for the latter products in some parts of Germany and France, but is now probably quite superseded for this purpose by richer materials, as bituminous lignite, shale, etc. The cessation of this industry involved also that of the recovery of ammonia by the same process.

Sometimes peat has been treated in specially constructed gas-producers, where the ammonia is washed out from the gas before using the latter for heating purposes. Such a "gazogène distillateur," constructed by Lencauchez, is described and figured in C. Vincent's *Industrie des Produits ammoniacaux*, p. 82; but the recovery of ammonia in this case must proceed

on the same lines as that proposed for gas-producers in general (see later on, under section K), and is equally unremunerative in most instances.

H. Grouven has made a special study of the recovery of ammonia from peat, especially that obtained from certain kinds of moor-lands ("Bruchmoore" and "Grünlandmoore"), which sometimes contains up to 3·8 per cent. N. The principle of Grouven's process (Ger. Ps. 2709, 13718, 18051) is, mixing the damp peat with chalk (in order to fix the sulphur), heating this mixture in upright cylinders by means of the gases remaining from the subsequent stages of the process, and passing the gaseous products of this dry distillation through a "contact substance," consisting of peat, chalk, and clay in equal proportions, moulded into the shape of drain-tiles, and heated in upright cylinders to a proper temperature. Here the nitrogen, under the influence of the incandescent aqueous vapour, hydrocarbons, and hydrogen given off in the first cylinders, is, to a great extent, converted into ammonium carbonate, which is condensed by calcium sulphate and thus converted into ammonium sulphate, or else by strontium sulphate (Ger. P. 34086).

Grouven's process was taken up by a company, and prolonged experiments on a large scale were made with it, but without pecuniary success, in spite of the then high price of ammonia. The question of utilizing the very large quantity of nitrogen contained in peat is therefore not yet finally solved, as it would not stand competition with the processes where ammonia is a by-product.

Rüderer, Loé, and Gumbart (Ger. P. 53844) combine the recovery of ammonia and acetic acid from peat with that of charcoal, but offer no peculiarity in the treatment for ammonia.

According to Kuntze,[1] on distilling peat, part of the nitrogen escapes as nitrates and pyrrol, and pyridine bases, amines, etc.; later on as ammonium cyanide and very little ammonia. A considerable formation of ammonia is attained only by superheating with steam on a large surface of hot, porous material containing much lime. Even then most of the nitrogen remains in the coke, and is convertible into ammonia by superheated air, saturated with steam. This he effects in the apparatus

[1] Ger. P. 62589; *Chem. Ind.*, 1892, p. 378; 1893, p. 340.

shown in Figs. 217 and 218. A is the distilling-chamber, *k* flues for heating this; *g* a number of bell-shaped cast-iron vessels which allow the vapours, but not too solid matter, to penetrate into the centre of the retorts. The partition *a* divides the upper drying space from the lower distilling space. The steam produced in the former escapes by S, the vapours from the latter by B. The peat, after having passed through the retort and being converted into coke, is conveyed through W into the gas-producer G, where the coke is gasified by means of superheated, moist air. The vapours formed in A are aspirated through B into a retort, C, filled with porous tar-coke, containing lime and kept at red-heat. The tar, ammonia, and vapours formed here deposit part of the tar in the hydraulic main D, the other tar and some ammonia in the water-scrubber E, the rest of the ammonia in the acid-washer E^1, and the volatile hydrocarbons in the oil-scrubber F; the remaining gases are forced through X into the retort fires. The gas-producer G furnishes gas rich in NH_3, which is carried away by H, serves for heating air in L, and is conveyed into chamber K, in which water is splashed about by paddles. Here the gas is cooled down to 100° C. and leaves dust behind, containing a little ammonia, whilst the bulk of the ammonia is recovered in the sulphuric-acid scrubber Q. The gases are deprived of most of the steam contained therein by cooling down to 30° C. by a spray of cold water in scrubber R, and are now sufficiently dry to be blown through O into the fire by means of blower *y*. The water from R, which is at a temperature of about 80° C., is pumped on to another scrubber T, into which air is forced by blower Z, and is thus reduced to 70° or 80° and saturated with moisture. The water thus cooled returns to R; the moist current of air is superheated to 200° or 300° and blown through

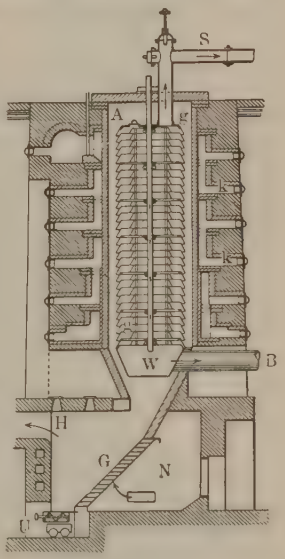


FIG. 217.

M on to the step-grate N, where it unites with the superheated steam from A, aspirated through S. The worm U constantly removes the ashes from the producer G, in proportion as the coke is burned. The angle of the step-grate N is sufficiently steep for the coke to sink down continuously from A.

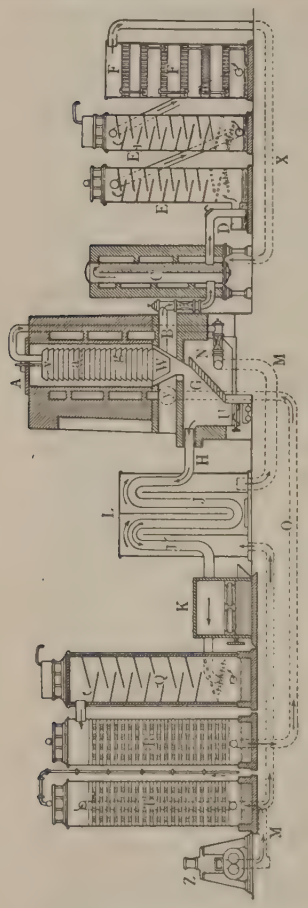


Fig. 218.

Pieper (Ger. P. 87061) first dries and slightly distils the peat in a revolving retort and then heats this to a very low red-heat, with introduction of steam. This produces CO_2, H_2, and NH_3. The NH_3 is absorbed by sulphuric acid, the remaining gas serves for heating. Later on, Pieper, together with Fellner and Ziegler, improved this process (Ger. P. 93705) by separately treating the gases from the distilling and steaming stages. After the first distillation the gases, containing two-thirds of all the ammonia, are by means of a valve conveyed into another channel; they are passed through a scrubber and contain merely H_2, CO, CO_2, and NH_3, so that they can be at once worked for pure ammonia preparations, whilst the gases from the first stage contain too much tar and must be treated in a more complicated manner.

Fig. 219 shows the furnace used for the above process. The cylindrical retort A revolves in furnace B; C, inlet for steam; D, outlet for gases; 1, 2, stuffing-boxes; 7, 7, flanges resting on rollers 8, 8, turned by the cog-wheel 9; 10, carrying-worm, working in the case 11. If the retort is turned 180° from the

position shown in the figure, neck 12 connects with the charging-funnel E. As shown in the figure, the retort is discharged into the carrier F. The heating takes place by gas, entering through H and *h* into the mixing and inflaming chambers N and b_2, together with heated air through G. The mixture travels through b_3 and b_4 into chamber *b*; the fire-gases travel through b_5 and b_6 before escaping through b_7, where the heating of the

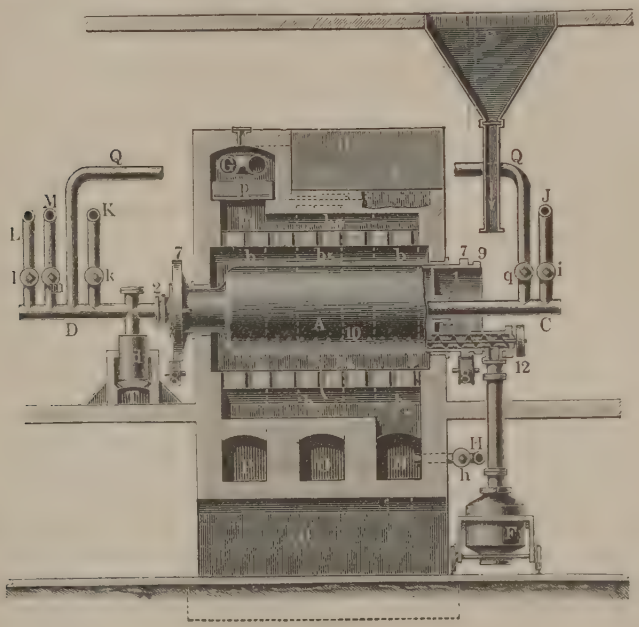


FIG. 219.

air takes place. The steam-pipe C is connected by *i* with pipe J, for superheating it. The outlet D can be connected by *k*, *l*, *m* with the pipes K, for steam (during the drying stage), L for gases of the distilling stage, M for the mixture of water-gas and ammonia during the last stage. A number of such retorts can be systematically connected.

An English patent of Pieper's (B. P. 28190, 1896) prescribes a series of six retorts, connected with one another for continuous working by means of steam superheated to 500° C.

An Austrian patent (No. 145374), for obtaining ammonia in coking peat, has been granted to M. Ziegler.

Woltereck obtained a B. P. 16504, of 1904, for the production of ammonia from peat by means of passing air and steam over or through it at a carefully regulated temperature. An improvement on this is his process (B. Ps. 28963 and 28964, of 1906), which provides for retaining the tar formed in the process, and which has an injurious effect on the quality of the produced acetate of lime and sulphate of ammonia, by passing the hot gases through a scrubber containing hot hydrocarbons of a high boiling-point in a liquid state, whereby the bulb of the tar is removed without simultaneous condensation of the water.

In *Chem. Trade J.*, vol. 42, p. 143 (1908), it is stated that works for carrying out the Woltereck process are now in course of erection in the north of Ireland, near Carnlough Harbour, for an annual output of at least 5000 tons of sulphate of ammonia by that process. In trials on the large scale work was continuously carried on for several weeks; 585 tons of moist peat (containing about 200 tons of dry substance) were passed through the furnace, and for every 100 tons of dry peat a *minimum* of 5 tons sulphate of ammonia was obtained, at a *maximum* cost of £5, 8s. 3d. per ton. The moist peat is delivered into hoppers, and from these by means of automatically working sliding-doors into the furnace, through which passes a blast of air, charged with water vapour, at a regulated temperature. The gases contain paraffin tars, acetic acid, and ammonia. They are passed first through a hot scrubber, described in the patent, where the tar is retained, then through a tower, fed with a hot solution of soda or milk-of-lime, where the acetic acid is absorbed in order to be afterwards utilized, and lastly through an acid tower, where they meet a stream of hot sulphuric acid. After this is completely neutralized, the solution of sulphate of ammonia (which forms the principal object of the process) is further concentrated and allowed to crystallize. The oil is drawn off from the paraffin tower, when a sample solidifies on cooling. It is then subjected to distillation to remove the lighter oils, and a crude paraffin wax, worth £4 per ton, remains without further purification. The acetate solution from the alkali tower is evaporated to dryness and distilled with sulphuric or hydrochloric acid, to obtain concentrated acetic acid, or is

subjected to dry distillation to obtain acetone. The ashes contain potassium salts and phosphates, and can be used for manurial purposes. The [unnamed] reporter considers the Woltereck process, which is worked by the Sulphate of Ammonia Company, Limited, to be the most economical process yet discovered for the manufacture of nitrogenous plant-food, and a great benefit to the inhabitants of the extensive tracts of land occupied by peat bogs, of which there are more than 2,800,000 acres in Ireland. Enormous peat moors also exist in the United States, Canada, Newfoundland, Sweden, Norway, Russia, and Germany (in Prussia about 5,000,000 acres, in Baden 75,000, in Bavaria 150,000 acres) hitherto almost entirely useless (cf. *supra*, p. 861).

A very favourable report on the Woltereck process has been made by the United States Consul at Birmingham (*Chem. Trade J.*, 1908, xliii., p. 224).

In a paper sent to the French Academy and read on 21st December 1908 (*Comptes rend.*, 1908, i., 124), Woltereck reports that he has found the nitrogen to accumulate in the residue to such an extent that it greatly exceeds the percentage of nitrogen in the peat employed. This was observed after 4 hours' working, but after 6 hours the percentage of nitrogen again diminished, ultimately down to half of the original quantity (*Comptes rend.*, 147, p. 1402; *Chem. Centr.*, 1909, p. 426).

Frank and Caro, in the discussion quoted *supra*, p. 838, altogether deny the accuracy of the statements made by Woltereck on the results of his process, more particularly his assertion to have obtained NH_3 from atmospheric nitrogen, in addition to that produced from the nitrogen of peat itself, and they point out that the caloric energy of the peat is very incompletely utilized in the Woltereck process, which not merely furnishes no excess of heating-gas, but requires more fuel than that afforded by the peat treated.

Ireland and Sugden (Ger. Ps. 175401 and 180141) pass air and steam over heated peat (or coke, lignite, coal, etc.), at temperatures not above 500° C. In this case the carbon burns slowly, without visible glow, and hydrogen is formed, which in the nascent state combines with the nitrogen of the air. Since the heat of reaction is sufficient to maintain the process without heating from without, their Ger. P. 176616 states that, after the reaction has set in, a mixture of air and finely divided water is

to be introduced at the ordinary temperature. According to their Ger. P. 180141, coke, charcoal, lignite, wood, etc., may be used in lieu of peat. The optimum temperature is 400°, but temperatures between 300° and 500° C. give commercially utilizable results. Besides ammonia, also tar, hydrocarbons, acetic acid are formed, and may be utilized.

In a further German patent, No. 205006, Ireland and Sugden prescribe dehydrating the peat mechanically down to 65 to 70 per cent. water, and passing the mixture of atmospheric air and water in the shape of spray or steam over it at a temperature not exceeding 500° C. That partial dehydration of the peat is supposed to increase the yield of ammonia, and to facilitate a constant temperature in the retorts.

Guillot and Brisset (Fr. P. 375792, of 1907) burn the peat in kilns, like lime-kilns, with limited access of air, so as to make the combustion slow, with or without injection of steam, and bring the gases into contact with suitable absorbents, liquid or solid, such as superphosphates, for absorption of the ammonia. In their Fr. P. 375792, they describe a special kiln for that purpose.

Müntz and Girard (B. P. 16162, of 1906) obtain nitrate of lime by impregnating peat, arranged in beds, with carbonate of lime and ammoniacal salts, so as to form a progressive nitrification and effecting the double decomposition of the nitrate of lime, obtained by the preceding treatment, with carbonate of ammonia, produced by the distillation of the peat.

Dromain (Fr. P. 392979, of 1907) constructs flues in the peat-bog itself or its immediate vicinity, in the shape of simple trenches covered with iron plates, and in these the peat is burned. The flues extend to the ammonia-recovery plant, and artificial draught may be necessary, if the distance be great; they are packed with dry peat, overlaid with wet peat.

Another way of utilizing the vast stores of peat in various countries is before us in the application of the Mond gas-process, described *infra*, p. 893. Peat by itself is not a very good object for destructive distillation, and A. Frank, in *Z. angew. Chem.*, 1898, p. 17, expressed himself very sceptically as to the fate of all processes for obtaining ammonia, etc., by the distillation of peat. But just the same distinguished practical chemist has later on pointed out that peat, when having been lying long enough in

heaps, might be gasified, in order to supply power for central electric stations. This proposal has become much nearer to fulfilment by the observation, made by N. Caro and the English Mond Company, that peat can be easily treated in Mond producers even when containing up to 50 per cent. water, and that in doing so 70 to 80 per cent. of the nitrogen contained in the peat can be obtained in the form of sulphate of ammonia, together with a very pure and uniform gas, eminently adapted for driving gas-motors. Bavarian peat, for instance, contains about 0·5 per cent., sometimes, however, up to 3 per cent., nitrogen. The latter would pay for the Mond treatment by the ammonia alone, leaving the gas and the power obtainable by it free of expense.

The publications by Dr Nikodem Caro on that subject are found in *Z. angew. Chem.*, 1906, p. 1569; *Glückauf*, 1907, p. 879; *Mitt. d. Ver. z. Förder d. Moorkultur*, 1907, p. 295; *Torflager als Kraftquellen*, Danzig, 1907; *Die Stickstofffrage in Deutschland*, Berlin, 1908.

A. Frank, in *Z. angew. Chem.*, 1908, p. 1597, reports on the results obtained with the Mond-Caro process in working-up raw peat, with 40 or 50 per cent. water, at Sodingen, in Westphalia. This peat contains on the average 1·05 per cent. nitrogen and 3 per cent. ashes. When working-up 45 tons per day, they obtained per 1000 kg. dry peat up to 2800 cbm. gas, containing 17·4 to 18·8 volume per cent. of CO_2, 9·4 to 11 of CO, 22·4 to 25·6 of H_2, 2·4 to 3·6 of CH_4, and 42·6 to 46·6 of N; calorific power 1400 calories per cubic metre, equal to a yield of 1000 actual h.p. hours per ton of dry peat. The yield of ammonia was up to 40 kg. sulphate per ton, *i.e.*, nearly four times as much NH_3 as the yield from real coal at gas-works and coke-ovens. When using peat, with 1 or 1·1 per cent. nitrogen at a price of 2 mark per ton in the damp state (50 per cent. water), with good wages and 15 per cent. for interest and amortization, a plant of 1000 h.p. supplies the h.p. per year at 40 to 50 mark, equal to the cheapest water-power in Scandinavia or Switzerland. In the case of "green-land" moors, with 1·5 to 2·0 per cent. N., the NH_3 pays all expenses and the power costs nothing. In this way the German moors, which cover $2\frac{1}{4}$ million hectares (say 5 million acres), could be made to yield power to the amount of 3 million h.p.

In the *Chem. Trade J.*, 1909, vol. 44, p. 81, it is claimed that the process in question is entirely a British invention, Messrs Frank and Caro being merely the consulting chemists for the German Mond Gas Company (the branch of the British Power Gas Corporation), and having published some results under their own name.

Frank and Caro (cf. *supra*, p. 868) energetically object to this way of stating the case. The Mond Gas Corporation (with which they are in most friendly relations) at their Staffordshire works do not gasify peat, but coal, by the "Mond gas-process," described *infra*, p. 893, and do not, like Frank and Caro, distribute electricity, but gas. The applicability of their process to partially dried peat has been proved by Caro at the Stockton works of the Mond Company, and only subsequently the Mond Company has taken up the process.

Ekeberg (*J. Soc. Chem. Ind.*, 1909, p. 511) asserts that by the "wet carbonizing process" 79 per cent. of the peat nitrogen can be converted into ammonia.

I. Ammonia from Bituminous Shale.

The distillation of bituminous shale for the purpose of obtaining oils and paraffin is a very important industry, and has attained very large proportions, especially in Scotland, where a suitable raw material is abundant. In converting the oils, ammoniacal liquor is also obtained. Many of the processes latterly proposed for the recovery of ammonia from coal (see under section K) equally apply to bituminous shale, and need not be described here. We will mention only the patent of Playfair (B. P. 3977, 1882), who mixes with the shale, before introducing it into retorts, an alkali or alkaline earth, for the purpose of increasing the proportion of nitrogen given off as ammonia; and that of A. Neilson and J. Snodgrass (B. P. 4902, 1885), who after having worked off the whole or nearly the whole of the oil in the ordinary way, either in horizontal, or vertical, or inclined retorts, introduce a mixture of air and steam, all external heating being discontinued. The air burns the carbonaceous matter remaining in the retort, and the increased heat causes the evolution of a large amount of ammonia in addition to that obtained in the primary distillation.

In the preceding section we have noticed several processes

applicable to peat and coal as well as to shale. The recovery of ammonia from shale is treated at length by Beilby (*J. Soc. Chem. Ind.*, 1897, p. 876), Redwood (*ibid.*, 1894, p. 108), Henderson (*ibid.*, 1898, p. 984), Heusler (*Berl. Ber.*, 1897, p. 2743; *Z. angew. Chem.*, 1898, p. 65), Henriques (*Chem. Rev.*, 1898, p. 61), and especially in a masterly way by Boverton Redwood ("A Practical Treatise on Mineral Oils and their By-products," London, 1897). We need not go into particulars here, as the recovery of ammonia from shale resembles very much that from coal (section K).

The processes in which the yield of ammonia from bituminous shale is increased by means of steam, which apply just in the same manner to coal, will be dealt with later on, *sub* K, No. 2.

The following table is found in the *Forty-third Annual Report on Alkali, etc., Works*, p. 164.

Year.	Total shale mined in the United Kingdom.	Sulphate of ammonia recovered from the shale.	Yield in lb. per ton of shale mined.
	Tons.	Tons.	
1897	2,223,745	37,153	37·4
1898	2,137,993	37,264	39·0
1899	2,210,814	38,780	39·3
1900	2,282,221	37,267	36·6
1901	2,354,356	40,011	38·2
1902	2,107,534	36,931	39·3
1903	2,009,602	37,353	41·6
1904	2,333,062	42,486	40·8
1905	2,496,785	46,344	41·6
1906	2,546,522	48,534	42·7

K. Ammonia from Coal.

Quite apart from the nitrogen forming four-fifths of our atmosphere, there is an enormous quantity existing in the form of organic substance and of products emanating from its decomposition. But for all practical purposes this is not of any great importance as a source of ammonia compounds in comparison with *coal*. Although only a small proportion of the nitrogen from coal is utilized in the shape of ammonia, the great bulk of our requirements of ammonia is supplied from this source.

The quantity of nitrogen in coal is very much greater than that contained in the fresh vegetable matter which forms its original material. Such vegetable matter rarely contains more

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than 0·1 per cent. N, whilst in coal we find from 10 to 20 times as much. This excess of nitrogen may have been partly absorbed from the atmosphere in the shape of ammonia (p. 861), but in all probability much of it represents the remains of the animals which lived during the growth of the coal-forming forests or swamps; just as we must attribute the same origin to the nitrogenous substances contained in bituminous shales.

The amount of nitrogen in coal varies from about 1 to 2 per cent. According to Dr C. Meymott Tidy (communication to the Author), coal contains:—

From Wales . . .	0·91	per cent. N.
„ Lancashire . . .	1·25	„
„ Newcastle . . .	1·32	„
„ Scotland . . .	1·44	„

W. Forster[1] obtained:—

From Welsh anthracite .	0·91	per cent. N.
„ English coal .	1·66 to 1·75	„
„ Scotch cannel . .	1·28	„

Knublauch[2] found in five Westphalian coals from 1·215 to 1·612 per cent., in two English coals 1·102 and 1·443 per cent. N.

E. Schilling ("Inaugural Dissertation") shows that most previous estimations of nitrogen in coal, made according to the method of Dumas or with soda-lime, are inaccurate, in which he agrees with Forster and Schmitz (*Stahl und Eisen*, 1886, p. 47). By Kjeldahl's method he obtained the following results:—

Westphalian coal (Consolidation) .	1·50-1·49	average	1·50 % N.
Saar coal (Heinitz I.)	1·09-1·02	„	1·06 „
Silesian coal (Louise)	1·38-1·35	„	1·35 „
Bohemian coal (Littiz)	1·38-1·34	„	1·36 „
Saxon coal (Bürgergew) . . .	1·25-1·15	„	1·20 „
English (Bolton gas)	1·49-1·40	„	1·45 „
Pilsener cannel coal (Plattenkohle) .	1·51-1·46	„	1·49 „
Bohemian lignite (Falkenau) . .	0·56-0·48	„	0·52 „

Generally the nitrogen increases as the oxygen decreases.

Only a small proportion of the nitrogen contained in coal is utilized in the shape of ammonia. More than 90 per cent. of the coal consumed in this and other countries is used in such a way that the recovery of ammonia from the products of combus-

[1] *Proc. Inst. Civ. Engin.*, lxxvii., part iii., p. 23.
[2] *J. Gasbeleucht.*, 1883, p. 440.

tion is nearly or altogether impossible; and of the remaining 10 per cent., only that portion is really fully utilized for the production of ammonia from which coal-gas is manufactured; while the recovery of ammonia from coke-ovens, about which more will be said hereafter, is still comparatively little developed in most countries except Germany, but is showing a steady increase in Great Britain during the last few years, as the statistics to be given hereafter will show. A notable quantity of ammonia is also recovered at the Scottish blast-furnaces fed with raw coal (*cf.* later on).

Since the great bulk of the ammonia compounds is obtained as a by-product in the manufacture of ordinary coal-gas, and the latter is unlikely to increase at the same rate as the consumption of ammonia, in view of the extension of the system of electric lighting, the question must necessarily arise: What will be the state of things if the demand for ammonia should exceed the supply? That emergency seemed inevitable at one time; and in consequence of this it was at once proved that a further enormous source of ammonia was present in the method of carbonizing coal which is practised in the production of *coke* for metallurgical purposes. The progress in this direction was not at first very rapid, owing to the sudden fall in the price of ammonia, which alone proved that the demand had not as yet exceeded the supply. When such is the case, however, coke-ovens will no doubt be generally reconstructed for the recovery of ammonia as well as of coal-tar, which is always produced at the same time as the former, and of which we have treated at length in Chapter II. Only when this second source of ammonia has been drawn upon to a large extent will it become probable that the further means for increasing the production of ammonia, as described in this chapter, will be turned to profitable account. But the utilization of the nitrogen even from coal burnt for household purposes and for raising steam, which is often thought of or spoken about, seems to be a matter of the remotest future; and it is less necessary to consider in this place, as not the slightest *practical* idea has yet been proposed as to how this could be accomplished. Nearly the whole of the nitrogen of the coal actually *burned* escapes in the elementary form, the temperature being much too high for the formation and existence of ammonia. We can only hope to obtain any considerable

amount of ammonia when coal is not properly burned, but submitted to *dry distillation*, as in gas- and coke-making, or by special agencies, of which we shall speak later on, but which as yet have found no profitable application.

Scheurer-Kestner[1] calculates that the recovery of ammonia in coking coal can only pay if the price of coal does not exceed 8s. per ton; hence the proposals for replacing the direct application of coal for firing by its conversion into coke, tar, ammonia, and heating-gas are of no value.

It is true that it would be a great boon to agriculture, if ammonia could be supplied for manurial purposes at a much lower figure than has hitherto been done. At present the major part of the nitrogen contained in chemical manures is the native nitrate of soda, which comes to us exclusively from Chili, and of which it is computed that about 300,000 tons annually are used for agricultural purposes. As nitrate of soda contains 16 per cent. N, the above quantity is equal to 48,000 tons of nitrogen, Taking the present annual production of coal in the whole world at 360 millions of tons, and its average percentage of nitrogen = 1·33, we find the nitrogen of the coal now consumed per annum to be = 4,800,000 tons, or just 100 times as much as that of the nitrate of soda utilized as manure.[2] Hence it would be sufficient to recover only one-hundredth part of the nitrogen of coals, in the shape of ammonia, to replace all the nitrate of soda used in agriculture.

If the manurial value of nitrate of soda and of sulphate of ammonia were exactly in the proportion of their percentage of nitrogen, 100 parts of the former would be equivalent to 78 parts of the latter. But the actual prices obtained in commerce do not correspond to this. Bunte[3] has discussed this question at length. He urges that, as a manure, nitrate of soda is certainly much more rapid and active, but ammonium sulphate, if slower, is more durable, and that the latter is not, like the former, washed out by the rain, and hence should be much more economical than nitrate in the long run. This seems to be borne out by the fact that the price of nitrogen in the shape of ammonia is nearly always higher than that in the shape of nitrate

[1] *Comptes rend.*, xcvii., p. 179.
[2] Cl. Winkler, *Jahresb. f. Berg- u. Hüttenwesen in Sachsen*, 1884.
[3] Schilling's *J. Gasbeleucht.*, 1885.

of soda, in the proportion of about 17 to 15. The annual importations in Germany were:—[1]

	1893.		1894.		1895.		1896.		1897.	
	Tons.	Price.	Tons.	Price.	Tons.	Price.	Tons.	Price.	Tons.	Price.
		M.		M.		M.		M.		M.
Ammonium sulphate	42,596	24	36,635	26	29,200	22	32,062	18	33,114	16
Ammonium carbonate, etc. . .	1,461	60	1,355	65	1,617	62	1,925	59	1,550	57
Nitrate of soda. .	384,710	17	404,562	17	459,515	15½	449,028	15	465,493	14½

(More recent statistics on ammonium sulphate will be given at the end of Chapter XIV.)

According to comparative experiments made by Wagner[2] with nitrate of soda and sulphate of ammonia, the action of ammoniacal nitrogen is, under the most favourable conditions, 90 per cent. of that of nitric nitrogen, but under ordinary circumstances they are equivalent. Hence, looking at the very large consumption of nitrate for agriculture, the latter will be able to utilize even a greatly increased quantity of ammonia salts.

1. Production of Ammonia in the Manufacture of Coal-gas.

In the dry distillation of coal, as practised at the gas-works, for the main purpose of obtaining illuminating-gas, it is necessary, in order to purify the gas, to subject it to cooling and washing with water ("scrubbing"). In this process two products are obtained from the gas—an oily and an aqueous substance, which, by settling in tanks, separate from each other, and form *tar* and *gas-liquor*. The former has been treated of at length in the preceding part of this book. The latter, which is always obtained along with tar, comes alike from the hydraulic main, the condensers, and scrubbers; the liquor from the hydraulic main, on account of the temperature, being poorer

[1] The prices given denote marks (=M.) per kg.

[2] *J. Gasbeleucht.*, 1892, p. 601.

than that from the scrubbers. Probably in every gas-works all the liquors are united, and either sold or treated in common at the works. Some liquor always remains incorporated with the tar, and is obtained in further settling and distilling it (pp. 314 and 358); but this is comparatively a small quantity, and is generally run to waste by such of the smaller tar-distillers who have not at the same time a contract for gas-liquor.

Some more ammonia condenses in the oxide-of-iron purifiers, and is hence contained in the "spent oxide."

A description of the condensers and scrubbers used at gas-works, of which there is already a very large variety in existence, does not enter within the scope of this treatise, as that subject belongs to gas-making proper. (Something will be said on this head in the section on coke-ovens.) We will, however, mention that by "virgin gas-liquor" is understood to be that which condenses from the gas in the hydraulic main and the air-condensers, and which is sometimes, but rarely, collected by itself, without mixing it with the other liquor obtained in the scrubbers, by washing the gas with water or weak liquor. Generally all the liquor runs into the same tank.

Yield of Ammonia in the Manufacture of Coal-gas.

We have seen (p. 872) that coal contains from 1 to 2 per cent. of nitrogen. But in the process of dry distillation nothing like the whole of this nitrogen escapes in the form of ammonia. As early as 1863, A. W. Hofmann stated that coal, in carbonizing, only yields one-third of its nitrogen, two-thirds remaining in the coke. We cannot wonder at this, if we consider that some of the well-known products of the distillation of coal-tar of the highest boiling-points, as carbazol and its congeners, contain 6 to 8 per cent. of nitrogen. Dr Tidy remarks that the four descriptions of coal, whose percentage of nitrogen is stated on p. 872, if all their nitrogen reappeared in the gas-liquor, would yield per ton of coal from 142 to 226 gallons of liquor at 4° Tw.; while in practice rarely more than 45 gallons is obtained, usually only 25, in London about 13 gallons.

W. Foster[1] showed that, of 100 parts of nitrogen contained

[1] *J. Chem. Soc.*, xliii., p. 105.

in coal, there were obtained, in a laboratory experiment,

14·50	parts	as ammonia.
1·56	„	as cyanogen.
35·26	„	in the elementary condition (as part of coal-gas).
48·68	„	remaining in the coke.

Watson Smith[1] found that coal-tar, which Foster neglects in his calculations, contained 1·667 per cent. N (pitch containing 1·595, and coal-tar oils about 2 per cent.); that is, not quite 0·1 per cent. N calculated upon the coal from which the tar is derived. In coke, he found :—

Ordinary gas-retort coke	1·375	per cent.	nitrogen.
Beehive coke	0·511	„	„
Coke from Simon-Carvès ovens	0·384	„	„

This shows that much less nitrogen is driven out of coal during the short process of gas-making than during the long-continued processes used in the manufacture of metallurgical coke.

Cl. Winkler (*Jahresber. f. Berg- u. Hüttenwesen in Sachsen*, 1884) quotes results of an experiment made in coke-ovens, where 28·7 per cent. of the nitrogen of the coal employed remained in the coke, and 71·3 per cent. escaped with the gases.

The total yield of gas-liquor obtained from various descriptions of coal has been stated (*supra*, pp. 28 and 29). It is generally assumed that a production of 20 lb. ammonium sulphate from a ton of coal is a fair yield.

Brunet (*J. Soc. Chem. Ind.*, 1899, p. 568) was able to increase the yield of ammonia from 4·10 to 4·83 lb. per ton of coal by simply keeping a layer of water at least 3 ft. deep on the surface of the tar in the tanks.

Knublauch[2] found, in three cases, that 31 to 36 per cent. of the nitrogen contained in the coal remained behind in the coke. Of the total nitrogen contained in five descriptions of Westphalian coal, only from 10·7 to 13·7 per cent. was recovered in the shape of ammonia; of two English coals, 9·39 to 24·34 [?] per cent. He estimates that of 100 parts of nitrogen there is recovered—

In the coke	31	to	36	parts.
As ammonia	10	„	14	„
As ferrocyanide in the spent oxide	1·5	„	2	„
In the tar	1·0	„	1·3	„

leaving about 50 parts of elementary nitrogen in the coal-gas.

[1] *J. Soc. Chem. Ind.*, 1883, p. 438. [2] *J. Gasbeleucht.*, 1883, p. 440.

Guéguen and Parent[1] do not give any useful information on this subject.

E. Schilling ("Inaugural Dissertation") found the percentage of nitrogen in real coal = 1·22 to 1·39, in Bohemian Plattenkohle = 1·00, in browncoal = 0·58; but with this should be combined the yield of coke, which varied from 40·5 to 74·2 per cent. of the coal; and we thus get the following table respecting the distribution of the nitrogen in coal:—

I. 100 *parts of Coal contained*

Nitrogen.	West-phalian.	English (Bolton).	Silesian.	Bohe-mian.	Saxon.	Saar.	Bohem. Cannel	Bohem. Brown-coal.
Total . .	1·50	1·45	1·37	1·36	1·20	1·00	1·49	0·52
Left in coke	0·96	1·02	0·95	0·77	0·86	0·85	0·56	0·23
Volatilized .	0·54	0·43	0·42	0·59	0·34	0·21	0·93	0·20

II. 100 *parts of Nitrogen reappeared*

In the coke .	80	72	70	69	64	57	44	38
Volatilized .	20	28	30	31	36	43	56	62

In order to test the actual yield of ammonia, E. Schilling made a large number of experiments at the Munich gas-works with a working retort specially fitted up for this purpose, but otherwise working under the normal conditions of gas-making and at a temperature of 1160 to 1220 C., as determined by Prinsep's alloys. He always made corresponding experiments without and with addition of lime, employing 2½ per cent. of the coal (Cooper's process). The table on p. 880 embodies his results.

This table most clearly shows that the coal containing most nitrogen did not necessarily yield the highest proportion of ammonia; that even in real coal the proportion of nitrogen recovered in the shape of ammonia may vary from 6·4 to 17·4 of 100 total nitrogen, that is almost as 1 : 3; and that "liming" the coal has, in some cases, a very slight effect, and may even cause a decrease in the quantity of NH_3, whilst in other cases

[1] *Etude sur l'Utilisation pratique de l'Azote des Houilles*, etc. Paris, 1885 (L. Michelet).

its effect is very considerable, viz., an increase of 30·7 per cent. in the case of English (Bolton) and of Saxon coal. It stands to reason that among the infinite variety of English gas-coals the differences will be quite as pronounced.

By a special series of experiments on a working scale, Schilling completely disproved the statement of Guéguen and Parent (*cf.* p. 878) that the increase of ammonia by "liming" (cf. *infra*, p. 884) is due to the water of hydration of the lime increasing the quantity of steam present in the retort: the contrary is decidedly the case.

Schilling believes it probable that the greater or smaller proportion of the total nitrogen has some relation to the percentage of oxygen in the coal, those coals which contain less oxygen generally giving out more of their N as NH_3 than *vice versa*. But this observation did not hold good in all cases, and would certainly require more extended investigations to be corroborated.

By experiments on the small scale, Müller[1] found that only $\frac{1}{5}$ of the nitrogen of coal is recovered as ammonia, and that mostly during the later period of the distillation of coal. This is confirmed by Hennin,[2] who finds that the formation of NH_3 takes place principally about a temperature of 1000° C.; higher temperatures are not favourable, and below a bright red-heat the formation of NH_3 ceases, thus proving this to be a secondary product. The hydrogen necessary for its formation, according to this author, comes from the "constitution water" of coal, as verified by the fact that of the nitrogen of coal only 10 per cent. [?] is transformed into NH_3 in gas-retorts or coke-ovens, but 15 per cent. in blast-furnaces with steam-blast.

The opinion formerly prevalent,[3] that already at the comparatively low temperature of 780° C. a dissociation of ammonia takes place, has not been confirmed in practice; on the contrary, the formation of ammonia increases with the temperature. But according to Jicinsky,[4] the nitrogen of different descriptions of coal has a different inclination to combine with nascent hydrogen. In coke-making he found $\frac{3}{4}$ of the nitrogen to remain in the coke; of the remaining $\frac{1}{4}$, part escapes as free nitrogen or cyanogen, and only from 0·188 to 0·089 per cent.

[1] *Stahl. u. Eisen*, 1888, p. 82.
[2] *J. Gas Lighting*, 1892, p. 296.
[3] *Stahl. u. Eisen*, 1889, p. 482.
[4] *Fischer's Jahresber.*, 1889, p. 13.

Yield of Ammonia and Distribution of Nitrogen from various descriptions of Coal (Schilling).

	Silesian.	West-phalian.	Bohemian.	English.	Saar.	Saxon.	Bohemian Cannel.	Brown-coal.
100 parts coal yielded parts of NH_3, without lime	0·284	0·248	0·237	0·189	0·188	0·094	0·221	0·129
Ditto, with lime	0·298	0·276	0·227	0·247	0·209	0·173	0·229	0·126
Increase or decrease of NH_3 by liming, per cent. of total NH_3	+4·9	+11·3	−4·2	+30·7	+11·2	+84·4	+3·6	−2·3
Percentage of N given off as NH_3, without lime	17·4	13·6	14·2	10·8	14·8	6·4	12·4	20·7
Ditto, with lime	17·9	15·2	13·8	14·0	16·2	11·9	12·7	19·9
Percentage of N left in coke (without lime)	69·0	64·0	57·0	70·0	80·0	72·0	38·0	44·0
Percentage of N as free N, cyanides, and tar, without lime	13·6	22·4	28·8	19·2	5·2	21·6	49·6	35·3
Ditto, with lime	13·6	20·8	29·2	16·3	3·8	16·1	49·3	36·1
Total N per cent. of coal	1·37	1·50	1·36	1·45	1·06	1·20	1·42	0·52
Of 100 parts volatile N there appears as NH_3, without lime	56	46	33	36	74	23	20	37
Ditto, with lime	58	42	32	47	81	43	20	36

of the total N is recoverable as NH_3. This author gives a table of the percentages of a number of German and Austrian coals in nitrogen, recoverable ammonia, and tar, for which we refer to the original.

Cf. also Knublauch's later paper on nitrogen and nitrogen compounds in coal,[1] and that of Anderson and Roberts (*J. Soc. Chem. Ind.*, 1899, p. 1099).

The sulphate of ammonia found in the *flue-dust of lead-furnaces* by M. W. Iles (*Eng. and Min. J.*, 1899, lxviii., p. 576) and R. C. Canby (*ibid.*, p. 633) undoubtedly comes from the nitrogen contained in the fuel employed.

We subjoin some more recent statements. Drehschmidt (*J. Gasbeleucht.*, 1904, p. 682) obtained from English coal 0·176 to 0·364, from Westphalian coal 0·204 to 0·29, from Silesian 0·146 to 0·317 per cent. NH_3.

Teodorowitsch (*Gastechniker*, vol. xliv., part 8) quotes the yield of NH_3 obtained at the following gas-works per cent.: Cologne 0·23, Dantzic 0·25, Zürich 0·19, Düsseldorf 0·24, Basel 0·163, Nürnberg 0·139, Magdeburg 0·18.

The nominal yields of NH_3 obtained in different shapes are always rather higher when making sulphate than when turning it out as concentrated gas-liquor or liquor ammoniæ, because the commercial sulphate of ammonia is not quite pure and in lieu of 25·75 per cent. contains only 23 to 24 per cent. NH_3.

On the whole, we may say that good gas-coal should yield from 0·16 (as a mimimum) to 0·25 parts of NH_3 to 100 coal, 0·20 being a good average. But many, especially small works, get only 0·10 to at most 0·15 per cent. NH_3.

M. Mayer and V. Altmayer (*J. Gasbeleucht.*, 1907, 25) have investigated the conditions of the formation of ammonia in the destructive distillation of coal. The different quantities of NH_3 which coal yields at different temperatures depend in the first instance on the composition of the coal. Since NH_3 dissociates at a high temperature, its quantity must be all the less the larger the red-hot surface and the longer the time of contact with this. The presence of CO_2 and CO promotes the liberation of the nitrogen of the coal at high temperatures, but the NH_3, formed in the first instance is to a great extent split up into its elements, and this is promoted by the catalytic influence

[1] *J. Gasbeleucht.*, 1895, pp. 753, 769.

of iron or its compounds, wherefore a high percentage of ashes may be injurious to the yield of ammonia. The same coal yields less ammonia in horizontal than in vertical retorts, or in the coking process, since in horizontal retorts the gas travels above the coal along the hot surface of iron and thus the ammonia finds an opportunity for decomposing, whereas in vertical retorts it escapes in the centre through a comparatively cool kernel of coal. The maximum yield of ammonia in destructive distillation is at 800° C. At higher temperatures more nitrogen is removed as NH_3, but this is partly decomposed into its elements.

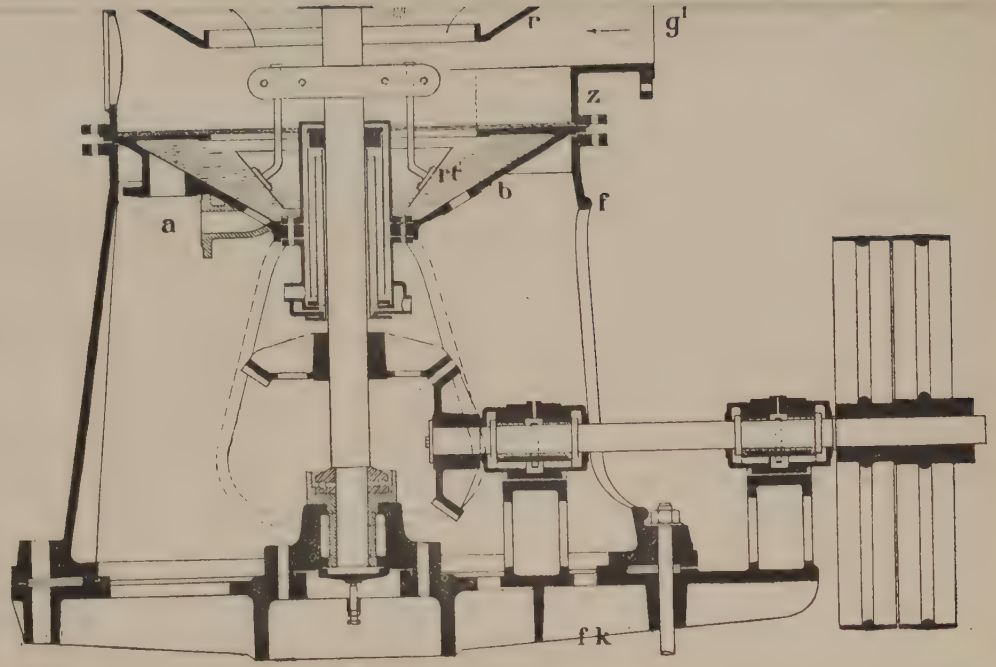
Fillunger (B. P. 11077, 1906; Fr. P. 365769) uses the same liquor over and over again, after driving out the NH_3 without addition of lime.

Special Processes for the Treatment of Coal-gas, etc., for Ammonia.

Koppers (Ger. P. 181346; Fr. P. 356600) suddenly cools down the gases to 40° or 45° C. Thereby, together with tar, most of the ammonia, especially the combined portion of it, is precipitated along with water, and thereupon the remainder of the tar is obtained in a tar-separator. The gases are now again superheated, eventually by employing them as a cooling agent for the hot gases, so that during the absorption of the remaining ammonia in acid the latter is not diluted by the condensation of aqueous vapour. From the ammoniacal liquor first obtained the ammonia is driven out by lime and is absorbed in the same acid which has removed the remaining NH_3 from the gases.

Feld (B. P. 966, 1904; B. P. 27567, 1907; U.S. P. 830983; Fr. Ps. 341614, 360528) separates from the gases first the tar fog in a liquid form by treating them at 100° to 200° C. with finely pulverized liquids, afterwards the aqueous vapour by cooling down to 40° C., by which process, he states, hardly any NH_3, either free or combined, is condensed. The gases, thus freed from tar and aqueous vapour, and containing nearly all the ammonia, are now absorbed in any suitable manner. In order to precipitate the tar fog to a liquid form, the hot, liquid tar itself is employed in the shape of a spray, brought into connection with the crude gases.

The same inventor, in two additions to Fr. P. 385628,



[To face page 882.

FIG. 220.

BIRMING

prescribes avoiding an excessive lowering of the temperature by the above process, for instance, by passing the mixing gas in a counter current against the crude, hot gas. He lowers the dew-point of distillation gases of any kind by addition of vapours or steam (*J. Soc. Chem. Ind.*, 1908, p. 677). *Cf.* also his Ger. P. 208288.

Feld's processes are very favourably reported on in the *Forty-fourth Report of the Alkali Inspectors*, pp. 62 and 63. It is stated that his process had been very successfully employed also for the removal of dust from blast-furnace gases, up to 99 per cent. with a three-chambered washer. At a number of continental gas-works, gas-producers, and blast-furnaces his process is now employed, also for removing lead fumes at lead-smelting works. At Mechernich an installation capable of dealing with 43 million cubic feet of furnace-gases per 24 hours has been ordered.

Feld's Washer is shown in Fig. 220. It consists of a number of superimposed sections. Each section consists essentially of a stationary basin of less diameter than that of the external casing. In the centre of the latter is a vertical shaft, *w*, to which revolution is imparted by gearing at the base of the washer. To this shaft is keyed an arrangement of concentric funnels, which dip into the liquid in the stationary basins. Rotation causes the washing liquid to rise in the funnels and to be thrown as a fine spray towards the outer casing; here baffle-sheets direct the ascending gas inwards, where it is intimately mixed with the washing-liquor in a very finely divided state. The descending liquid overflows from basin to basin. The power to drive the apparatus, even with hot tar as the extracting fluid, is very small.

In B. P. 27568, of 1908, Feld claims the lowering of the dew-point of distillation gases by the addition of heated gases to such an extent that the temperature of the gaseous mixture remains above the desired dew-point.

The same inventor (U.S. P. 851340; B. P. 18505, 1906), in the case of gases containing less than 1 mol. CO_2 to 2 mols. NH_3, treats the gas-liquor with calcium sulphate, partly suspended and partly dissolved in water. Gases containing CO_2 may be passed in at the same time.

When employing magnesium salts for taking the ammonia out of gases which contain also CO_2, Feld (Ger. P. 185419;

B. P. 26262, of 1905; U.S. P. 837045; Fr. P. 369258) adds to the washing liquid alkaline or ammonia salts, in order to prevent a solidification of the liquid during the absorption or concentration to a stiff paste, which otherwise easily happens both in the washer and in the ammonia stills when regenerating the washing liquid. The absorbing-process is then:

$$MgCl_2 + 2NH_4Cl + 2NH_3 + CO_2 + H_2O = 4NH_4Cl + MgCO_3;$$

the boiling-off process:

$$(a)\ 2MgCO_3 + 8NH_4Cl + H_2O = MgCO_3 . Mg(OH)_2 + 8NH_4Cl + CO_2;$$

$$(b)\ MgO . Mg(OH)_2 + 8NH_4Cl = 2(MgCl_2 . 2NH_4Cl) + 4NH_3 + CO_2 + 2H_2O.$$

The CO_2 becoming free in (*a*) may be separately caught.

Some of the processes described later on in this chapter for the recovery of ammonia from the products of destructive distillation might no doubt be employed in the treatment of coal-gas as well.

Processes for increasing the Yield of Ammonia in Gas-making.

1st. *By means of Lime.*—W. J. Cooper (B. P. 5713, 1882) mixes with coal, previous to its distillation, either lime, quicklime, carbonate of lime, or spent lime, the object being to obtain an increased production of ammonia, or of tar or gas. This process has been discussed by J. A. Wanklyn.[1] It is usually carried out by thoroughly mixing the slaked lime, produced from 2½ parts of quicklime, with 100 parts of coal, before charging this into the retorts. This "limed coal" is stated to yield a slightly larger fraction of its carbon in the form of volatile substances (tar and gas); also to yield a much smaller fraction of its sulphur in volatile forms, and better coke than that ordinarily obtained. In the discussion following Mr Wanklyn's papers the latter points were seriously contested. It was shown that the retention of sulphur in the coke causes a considerable loss in the value of the spent oxide, and that the quality of the coke is in reality deteriorated. But it cannot be doubted that one point urged by Mr Wanklyn is correct, namely, that by Cooper's process more nitrogen in converted into ammonia. A number of gas engineers testified to a substantial gain in

[1] *J. Soc. Chem. Ind.*, 1883, p. 438; 1884, p. 12.

ammonia; in one case it was doubled in quantity, the highest yield obtained on the large scale being about 9 lb. of ammonia (= 36 lb. ammonium sulphate) per ton of coal. Whether this gain of ammonia is or is not neutralized by the expense of "liming" and the loss of sulphur in the spent oxide, is a question which must be decided by local circumstances. Only a few gas-works introduced Cooper's process; and, according to information received by the author from highly trustworthy sources in 1886, there was but little prospect of its more general adoption, as the extra yield of ammonia is counterbalanced by several drawbacks. In fact, according to the *J. Gas Lighting*, 1902, p. 1392, that process had been abandoned everywhere except at Folkestone.

From the experiments made by E. Schilling (*vide supra*, p. 879) it appears that "liming" affects various kinds of coal very differently. Sometimes the NH_3 is slightly increased (from 3 to 11 per cent.), frequently even diminished (by 2 to 4 per cent.); a considerable increase was observed only twice, viz., 30·7 per cent. with Bolton gas-coal and 84·4 per cent. with Saxon coal. Schilling also refuted the assertion of Guéguen and Parent that the increase of NH_3 in "liming" is caused by the hydration-water of lime.

Knublauch[1] found that an addition of 2½ per cent. lime increases the yield of gas by 5 per cent., and decreases its quality of gas by 5 per cent. The yield of coke is slightly increased, but its heating-power on the whole remains the same. The quantity of tar is 10 per cent. less, and its quality is inferior, There is an increase of 20 per cent. NH_3. The H_2S is diminished by 1·4 per 1000 coal, and in so far the purifiers have less work to do. The crude gas contains 10 per cent. CO_2 more, but most of this is removed in scrubbing.

Walton Clarke[2] found an increase of NH_3 by 39·8 per cent. less H_2S and CO_2, with no loss in yield and illuminating-power of the gas. The coke did not suffer in illuminating-power, but its hardness falls below the allowable standard, as is explicable by the slaking of the lime on watering the coke.

2nd. *By means of Hydrogen.*—R. Tervet (B. P. 1842, 1883) passes hydrogen over coal, shale, etc., in the retorts during distillation, or over the coke remaining therefrom. The

[1] *J. Gasbeleucht.*, xxx., pp. 55 and 96. [2] *J des Usines à Gaz*, xi., p. 101.

hydrogen is to be obtained as in the manufacture of water-gas, or by passing coal-gas over highly heated coke. It should be used largely in excess of the quantity theoretically sufficient to combine with the nitrogen of the coke; and the same hydrogen is several times used over again in the retorts. This process is discussed at length in a paper by Tervet himself,[1] from which it appears that his experiments were made only on a minute scale. He obtained ammonia equivalent at most to 83 lb. of sulphate from 1 ton of coal; but when working with "somewhat larger quantities" (2 oz. of coal!) the results fell off from 39 lb. to 67 lb., and no experiment whatever seems to have been made on a working scale; nor is there any clue as to the probable cost of the process. We must therefore refer to the original for details.

3rd. *By means of Steam.*—The processes belonging to this class are hardly applicable to real illuminating-gas, and will therefore be treated separately later on (p. 888 *et seq.*). The proposal of Kenyon (B. P. 1016, 1886) may also be applied to ordinary gas-retorts.

Ammonia recovered from Coal-gas directly, without Scrubbers.

F. J. Bolton and J. A. Wanklyn (Ger. P. 16788) pass the crude gas, freed from tar, but not scrubbed, through a purifier in which superphosphate is spread out on trays; thus an ammoniacal manure is formed without having to collect and distil gas-liquor, and without wasting sulphuric acid. This process is extended by a further patent (B. P. 2709, 1882) to the gases from coke-ovens and blast-furnaces. These are passed through pipes into which superheated steam is injected, in order to remove the tar. In these pipes, plates of wire-netting or corrugated sheet-iron are placed longitudinally, to catch tar and soot. The gases are then passed through perforated trays, containing superphosphate, gypsum, or coke moistened with sulphuric acid, to condense the ammonia; if rich in ammonia, they are first passed over shallow pans filled with sulphuric acid.

Practical experiments made with this process have been described by Bunte.[2] The superphosphate employed was made from Mezillones phosphates, and was first neutralized with gas-

[1] *J. Soc. Chem. Ind.*, 1883, p. 445. [2] *Dingl. polyt. J.*, vol. ccxlv., p. 40.

liquor to prevent any free sulphuric acid from absorbing the heavy hydrocarbons of the gas. The gas was passed over this, after coming from the scrubbers, with 60 g. of NH_3 per 100 cbm.; after passing through the superphosphate the ammonia decreased to 3·4 g. In a second experiment, the scrubbed gas contained from 60 g. NH_3; when scrubbing was discontinued, 108 g. per 100 cbm.: the gas issuing from the superphosphate apparatus contained at first 8 or 9, later on 12 g.; with increasing saturation of the superphosphate, at least 50 g. NH_3. If this process were to be introduced on a large scale, it would evidently be necessary to provide a series of purifiers, worked methodically, like oxide-of-iron purifiers, so that the gas should always pass in the end through fresh superphosphate.

Vorster and Grüneberg (Ger. P. 21837) pass coal-gas over trays charged with a mixture of infusorial earth (*Kieselguhr*) of flue-dust and sulphuric acid, in order to retain ammonia. Another patent (Ger. P. 25466) claims the use of a large number of other porous materials for the same purpose.

A. P. Price (B. P. 6983, 1884) claims the use of sulphuric and sulphurous acid, and of potassium, sodium, or ammonia phosphate for retaining the ammonia present in coal-gas.

Cuyper (Ger. P. 70791) absorbs the NH_3 from gas by means of damp peat, which retains also the H_2S, and yields the free ammonia by heating to 40°, or at most 80° C.

Ammonia from the spent Oxide of Iron of Gas-works

is very frequently recovered by simple lixiviation, acidifying with sulphuric acid, and evaporation. Such sulphate is often very impure, and especially very frequently contains large quantities of sulphocyanides. Th. Richters (Ger. P. 15206) for this purpose washes or steams the spent oxide every time before it is regenerated, preferably by treating it with air in a box fitted with divisions. In this way the regeneration is combined with the recovery of ammonia, since the process of oxidizing the ferrous sulphide to oxide and free sulphur evolves so much heat that the ammonia is driven off, and can be washed out of the escaping air by means of acid.

The total production of ammonia at the German gas-works is estimated by Bunte for the year 1904 at 9000 tons NH_3, equal to 36,000 tons sulphate. Of this only

27,000 tons have been actually made; the remainder has found other uses.

2. Production of Ammonia by treating Coal or Shale with Steam.

We have seen (pp. 876 *et seq.*) that only a small portion of the nitrogen of coal is converted into ammonia in the ordinary process of gas-making, and that the greater portion remains behind in the coke. A similar thing happens in the distillation of bituminous shale, as carried out especially in Scotland. Hence have arisen a number of attempts at obtaining a much larger quantity of ammonia by special treatment. We may class among them already the processes enumerated in the last section; but while these still aimed at producing at the same time ordinary illuminating-gas as the principal product, we shall now speak of those processes which treat the coal for ammonia as a principal product, and obtain a gas not fit for lighting-, but only for heating-purposes, more or less like the well-known "water-gas." This arises from the fact that all these processes operate by means of *steam*. We treat, of course, not of the operation of steam for improving producer-gas generally, but only as regards increasing the yield of NH_3.

W. Young and G. T. Beilby (B. P. 5084, 1882) introduce coal-dross, shale, peat, etc., in a fine state of division into highly heated retorts, where it is consumed in an atmosphere of steam and air, with the production of a heating-gas rich in ammonia, along with undecomposed steam. This gas is cooled down to a certain extent, and the ammonia is then taken out by sulphuric acid, after which the gas is then ready to be used as fuel. G. Beilby has given a detailed description of this process.[1] Its principle is: distilling coal first in a current of steam, and burning the coke, which retains about 60 per cent. of the nitrogen, in a mixture of steam and air, the former being in such large excess as to preserve from decomposition the ammonia derived from the nitrogen of the coke. When this process is properly managed, ammonia is produced equal to from $\frac{2}{3}$ to $\frac{4}{5}$ of the nitrogen of the coal, or from three to four times as much ammonia as is produced by the most efficiently performed

[1] *J. Soc. Chem. Ind.*, 1884, p. 216; *cf.* also 1885, p. 220; and, Watson Smith's Report, *ibid.*, p. 472, which is reproduced here.

destructive distillation. This result, however, can only be obtained by the partial or total consumption of the carbonaceous residue, so that the process is only applicable to the production of gas, not of coke, from coal. One-half of the fixed carbon of coal is oxidized by the oxygen of steam setting free an equivalent amount of hydrogen. The gas obtained is very much richer in hydrogen than ordinary producer-gas, or even the gas from the Wilson producers, where steam is also used, and is therefore a more valuable fuel. This is proved by the following analyses :—

	Wilson gas.	Young & Beilby gas.
Carbon dioxide . .	7·14	15·40
Hydrogen . . .	12·15	34·53
Carbon monoxide . .	19·83	10·72
Methane	3·91	4·02
Nitrogen	57·24	35·33
	100·27	100·00

This principle has been carried out by two different forms of gas-producer.

The first form is designed for supplying the heat to shale-retorts. It consists of a vertical retort built of brick, closed by a door at the top, and provided with an exit-pipe which connects the retort with a system of mains and condensers. At its lower end the retort terminates in a closed fireplace as ashpit, with regulating doors or dampers. The dross or small coal is introduced by the top door, and, resting on the firebars, fills the retort from top to bottom. The upper part of the retort, being surrounded by flues through which fire-gases are led, is kept at a full red-heat. The coal in this part of the retort is distilled, and parts with gases and vapours, which pass away by the exit-pipe to be cooled and condensed. As the coke passes down in the retort, it is met by a current of steam, which is partly decomposed, burning the carbon, and producing ammonia and "water-gas," which pass off along with the other volatile products. When such coke as has escaped the action of the steam reaches the firebars, it is turned into carbon monoxide by a regulated admission of air. This red-hot carbon monoxide passes off by ports at the lower end of the retort, and is burned in the flues surrounding the shale-retorts. The gases from the upper

part of the retort, after having been deprived of their condensable constituents, are also returned and used in firing the retorts. By this system of firing, less fuel is used than by the open furnace, and the ammonia and tar recovered from the coal more than pay its first cost. About 200 of these retort-producers were then in use in Scotch oil-works.

The second form is for the production of gas for firing steam-boilers or for metallurgical operations. The shell of the retort is built of grooved bricks as before, but it is of circular section and of much larger diameter than the early retorts. The top is closed by a shallow hopper of cast-iron, with two small charging-doors; through the centre of this hopper a large iron pipe is led half-way down the retort. This pipe is for the exit of the gases, and passes up into a large dust-box which runs along the bench. From the dust-box the gas is conveyed by large pipes to the condensers and exhauster. The bottom of the brick retorts rests on an iron snout-piece, which is provided with a door at the outside of the setting. The steam and air are blown in at the front of this snout-piece. The gas and air for heating the setting are led up by pipes between the walls of the building, and are thereby heated before they take fire. The fire-gases surrounding the retorts are drawn downwards by chimney draughts, and before entering the main flues at the bottom of the setting they give up their heat to the iron snout-pieces, through which the steam and air are entering.

Gas Condensers and Scrubbers.—In carrying out the process of gasifying carbonaceous residues in excess of steam, a great deal of heat is carried away from the operation by the large quantity of gas produced. To recover a part of this heat, and to make it again available in the process, certain forms of regenerative condenser have been devised. In these, the hot gases from the retorts pass through tubes which are immersed in water or are kept wet by a shower or spray of water. The tubes are enclosed in a box or case through which a current of air is forced. The air becomes saturated with water-vapour to an extent depending on its own temperature and that of the wetted tube-surface. This saturated air, by the further addition of steam, is available for the incineration of the coal in retort gas-producers. As the principal consumption of heat in the vaporization of water is that portion which is latent in the

steam, the economy of this method of producing water-vapour from heat of comparatively low grade is very evident. Air at 65° C. takes up one-fourth of its weight of water, at 74° one-third, at 80° one-half, at 85° an equal weight, and at 93° twice its weight; it is therefore possible to raise into vapour large quantities of water by means of a comparatively small volume of air. Condensers of this construction had been working satisfactorily in the Clippens Company's works at Pentland for nearly two years (1885).

Beilby states that of 100 parts of the nitrogen contained in bituminous shales (amounting to about 1 per cent.) there is recovered in distilling them in the usual manner for the production of paraffin oils: 17·0 as ammonia in the watery distillate, 20·4 as alkaloidal tar, 62·6 in the residual coke. When the distillation was carried on first at a low red-heat, and the residue was afterwards subjected to a bright red-heat in the presence of steam, only 4·9 per cent. of the total nitrogen was left in the coke, 74·3 per cent. being recovered as ammonia, and 20·8 as alkaloidal tar. A certain proportion of air may be mixed with the steam without seriously reducing the yield of ammonia. This has the advantage that a certain amount of heat is generated within the retort, and less heat has to be supplied from the outside.

Ingenious as the system of Young and Beilby is, we can hardly expect it to make much way at the present prices of ammonia. It must also be considered that the conditions for producing a maximum of ammonia, and those for turning out the best possible water-gas, are opposed to each other. For the former, the temperature ought to be kept down, if possible, below 500°, since ammonia, under favourable circumstances, begins to be decomposed rather below 500°, and is fully split up at 780°. But in order to realize as nearly as possible the theoretical reaction of forming water-gas,

$$C + H_2O = CO + H_2,$$

the temperature ought to be at least 900° C.; below this the reaction

$$C + 2H_2O = CO_2 + H_4$$

gets the upper hand. In fact, the best temperature for the formation of good water-gas is about 1000°.

This difficulty can be overcome on the small scale by employing an excess of steam. H. Grouven, in his analytical process for estimating the percentage of nitrogen in organic substances, passes through the apparatus a quantity of steam equal to 20 or 30 times the weight of the substance. W. Foster (see below) used 16 times the theoretical quantity. This is evidently impossible to apply on an industrial scale; but Young and Beilby have found that by mixing steam and air, 60 or 70 per cent. of the nitrogen can be obtained on the large scale as ammonia, with an expenditure of only $1\frac{1}{4}$ parts of steam to 1 part of coal. That, however, the heating-gas obtained by their mode of operation is of a somewhat poor description, can be seen from the analyses quoted above.

It must not be forgotten (and Beilby, in the above-quoted communication, fully acknowledges this fact) that, as early as 1878, Grouven (*cf.* p. 862) had recognized that the introduction of superheated steam in carbonizing organic substances greatly increases the quantity of ammonia obtainable therefrom. Long after him, and also some time after Young and Beilby (whose patents date from 1881 and 1882), W. Foster[1] drew attention to the same fact. By using an enormous excess of steam (16 times the theoretical quantity) he was able to convert 61·6 per cent. of the nitrogen of coke into ammonia, 35 per cent. remaining behind, and 3·4 per cent. being unaccounted for. He assumes (but without any data to warrant this assumption) that on the large scale the amount of steam required would be "not unduly in excess of the theory." His calculations concerning the thermal value of water-gas are quite incorrect.[2]

Hennin,[3] who also blows an exactly regulated quantity of air and steam into red-hot coal, so as to keep the temperature constant at 1000 C., asserts that he obtains $\frac{1}{2}$ or $\frac{2}{3}$ of the nitrogen of the coal as NH_3, together with much tar and a good heating-gas, containing 38 per cent. H, 4·5 methane, etc., 20·0 CO, 10·5 CO_2, 27 N and O. [These results are incredibly high.]

A process, very similar to Young and Beilby's, has been patented by G. R. Hislop (B. P. 5252, 1882). H. Simon and Watson Smith (B. P. 4871, 1883) have patented the injection,

[1] *Proc. Inst. Civ. Eng.*, 1883-4, vol. lxxvii., part 3.

[2] Cf. *ibid.*, pp. 65 and 76. [3] *J. Gas Lighting*, 1892, p. 296.

into gas-retorts, coke-ovens, or gas-producers, of steam along with hydrocarbons in a liquid or gaseous state. Whilst the oxygen of the steam unites with the carbon, a portion of the hydrogen set free unites with the nitrogen of the partially decomposed coal, forming ammonia; a portion also of the hydrogen unites with the sulphur of the fuel, so that the quality of the coke is improved by this treatment. This process has only been carried out experimentally up to the present. A similar object is aimed at by the process of H. Kenyon (B. P. 1016, 1886).

A. French (B. P. 5945, 1885) claims the following invention:— Any material containing carbon, nitrogen, sulphur, and common salt or another suitable chloride, is heated in a kiln, air and steam being injected during the heating-process. The kiln is worked continuously. The reaction said to take place is expressed by the following equation:—

$$2NaCl + H_2SO_3 + 3H_2O + 2N + C = 2NH_4Cl + Na_2SO_4 + CO_2.$$

Nearly the whole of the nitrogen is said to be obtained as ammonium chloride, a small portion of it combining "with carbon and chloride, hydrogen, carbon monoxide, or sulphurous anhydride, to form various cyanogen compounds."

The Mond Gas-process.

We now come to a process which has during recent years taken such a considerable development that it is everywhere regarded with the greatest attention.

L. Mond (B. P. 3923, 1883), like the inventors quoted just now, utilizes the fact that a low temperature and the presence of steam in gas-producers are conducive to the formation of ammonia. Hence he introduces into the furnace a limited supply of air, loaded with water-spray or steam in large quantity. The resulting gases are said to be richer in hydrogen, and to have a higher heating-power, and the tarry matter to be richer and larger in quantity. The temperature may also be kept low by using air partly deprived of oxygen, *e.g.*, furnace-gases. The ammonia and tar are collected by cooling and condensing; or the ammonia may be absorbed without cooling by a solution

of calcium chloride or magnesium chloride, or by sulphuric acid. The principal novelty claimed is, charging the limited supply of air with so large an excess of steam or water that the temperature of combustion does not exceed a dull red-heat. In a

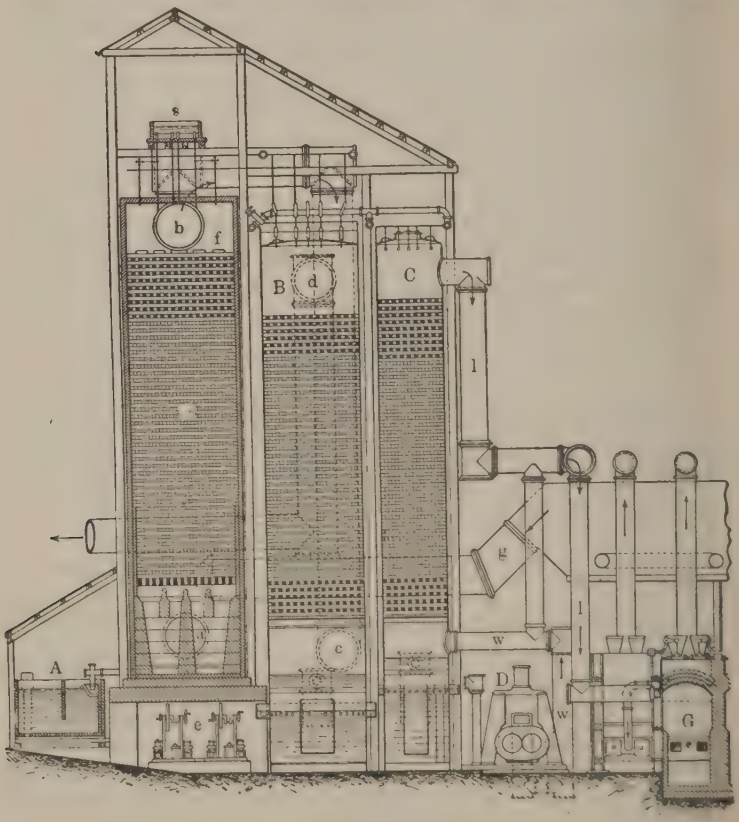


FIG. 221.

further patent (B. P. 8973, 1885) Mond describes special means for cooling and condensing producer-gas. He passes it through a scrubber, in which it is cooled to 40 by a current of water. This water, loaded with ammonia and tarry products, is afterwards cooled by another stream of water flowing in the opposite

direction; it is then again passed through the scrubber and again cooled, and so on, the same water being constantly used. The steam in the producer-gas being condensed by this treatment, a quantity of water equal to the condensed steam is drawn off at intervals, and from it the ammonia is recovered. To obtain the latter in the form of sulphate at once, the producer-gas is scrubbed with very dilute (2-per-cent.) sulphuric acid; the solution of ammonium sulphate thus obtained is used over again, fresh sulphuric acid being added after each absorp-

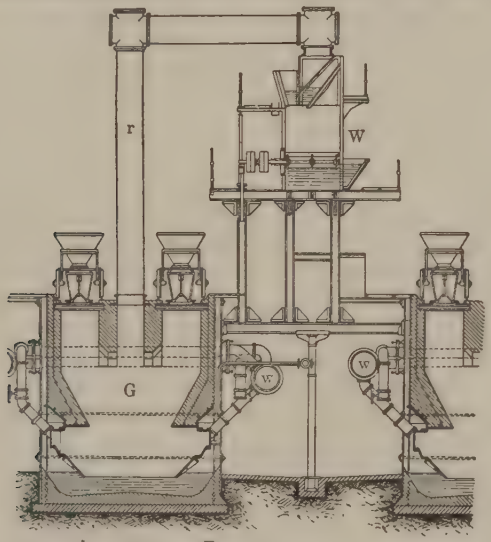


FIG. 222.

tion, to restore the original acidity. This operation is continued till a sufficiently concentrated solution of ammonium sulphate is obtained to separate the salt from it. The tar is separated in the usual manner, and the residual gases are used as fuel. This method is said to effect a saving of most or all the fuel now used for raising steam for the purpose of working gas-producers under the patents Nos. 3821 and 3923, of 1883 (the former of these patents does not refer to the recovery of ammonia).

Mond himself later on gave some interesting details concerning his process,[1] illustrated by figures (see Figs. 221 and 222).

[1] *J. Soc. Chem. Ind.*, 1889, p. 505.

The gas produced in the generators G is passed at a temperature of 450° or 500° C. through pipe *r* into the washers W, in which water is splashed about by paddles. Part of the water is evaporated, the remainder absorbs the ammonia and is run off from time to time to recover this. The tar condensed here is also occasionally removed. The gases leave the washer at a temperature of 100° and containing much steam, by *g*, and enter at *a* a tower, S, filled with perforated bricks, where they are deprived of the last ammonia by the solution contained in *s*. This is a solution of ammonium sulphate, of sp. gr. 1·33 to 1·36, containing 2·5 per cent. free sulphuric acid—no more, as this would act upon the tar and stain the liquor dark. When this issues from the tower, it passes a tar-separator, A, from which most of it is pumped back into *s* by pump *e*. Part, however, is freed from tar by treatment with heavy tar oil, and is evaporated in leaden pans with a steam-coil until the mass is a thick magma. This is centrifugalled, and after washing yields good, saleable sulphate of ammonia; the mother-liquor containing all the free acid is pumped back to the condensers.

When entering the tower S, the producer-gas contains 0·13 vol. per cent. NH_3; on leaving it, 0·013 per cent. It is at a temperature of 80° and completely saturated with steam. This is only condensed to water in *c*, where a stream of cold water converts the steam into water of 78°. At *d* the gas, now cooled down to 40° or 50°, leaves through *c* and is conveyed to the places where it is to be used. The hot water is first separated from tar and pumped on to a third tower, C, where it is cooled by air, forced in by the Root's blower D and pipe *w*, so that it can be again used in the scrubber B. The air is thus heated to 76° and saturated with steam, and is forced through *l* and *w* into the producer G, to which it supplies $\frac{2}{3}$ of the original steam, so that only $\frac{1}{3}$ has to be supplied by the exhaust of the main engine.

The gas-producers G have a rectangular section (6 × 12 feet) and are arranged in a series. The introduction of the air and the removal of the ashes take place at the shorter sides, which meet in the centre and are closed by a water-lute. The air enters under a pressure of 4 inches water; the ashes are also removed under water; but the air from pipe *w* enters above the water-level. The coal is fed in by hoppers near the exit-pipe *r*

in such a manner that the products of distillation must pass through red-hot coal, which gasifies much of the tar and keeps back the dust generated in the feeding process. The loss of coal in the ashes is only 3 or 4 per cent. of the total. The composition of the gas in the dry state is: 15 per cent. CO_2, 10 CO, 23 H, 3 hydrocarbons, 49 N. Its heating value is $\frac{3}{4}$ of that of the coal consumed, but its utilization is much better, since it can be burned with only 2 or 3 per cent. excess of oxygen. The steam raised is 85 per cent. of what could be raised by the coal if burned on a grate. Deducting the steam introduced into the producers and required for concentrating the ammonium sulphate liquor, the above percentage decreases to 75, but is raised to 80 per cent. by the tar.

In order to recover half of the nitrogen of the coal in the shape of ammonia, 125 tons of coal must be burned in lieu of 100 tons burned in the usual way. These 125 tons of coal furnish 4 tons sulphate of ammonia, which means that for 1 ton of sulphate, $6\frac{1}{4}$ tons of coal are lost. The value of this coal at Northwich is about £1, 15s.; adding the cost of extra labour, of sulphuric acid, etc., the cost of 1 ton sulphate of ammonia is from £4, 10s. to £5, that is, about half its average market price. Apart from this profit, there is the advantage of very regular firing by the gaseous fuel and of avoiding all smoke.

Thus the matter stood about the year 1890, when Mond's process, apart from his own works, had been introduced at very few other places, as it cannot be profitably carried out except on a very large scale, and as the ammonia in this way is recovered at the expense of greatly reducing the caloric effect of the producer-gas, so that the process could only pay at localities where coal is very cheap.

The Mond gas gives out only 1100 to 1200 g.-calories per cubic metre, and is therefore not to be compared to coal-gas, but only to producer-gas. Its direct use under steam-boilers is not very convenient. But the introduction of gas-motors has entirely changed this. In consequence of its purity and its practically constant composition, that gas is eminently adapted for gas-motors, as proved in practice. The wear and tear of the motors, otherwise a sore point, is reduced almost to a minimum.

The Mond process and its applications to various materials are treated at length in an important paper by Nikodem Caro

(*Z. angew. Chem.*, 1906, pp. 1569 *et seq.*). He sets out with a demonstration of the continuously increasing demand of nitrogenous matters for agricultural purposes, which is at present to a great extent supplied by Chilian nitrate of soda. The only important home source of nitrogen in Germany (and even more so in Great Britain!) is coal. Part of its nitrogen is already now recovered in the shape of sulphate of ammonia, of which Germany produces a considerable quantity (190,000 tons in 1905). She imported, however, in that year, still upwards of 20,000 tons of sulphate of ammonia,[1] besides 571,140 tons of nitrate of soda and 57013 tons of guano. Her total consumption of nitrogen in all shapes in 1905 was 150,000 tons; the yearly increase of consumption of nitrogen, which formerly amounted to 6000 tons, had then risen to 15,000 tons. The solution of the question how this great and constantly increasing demand of nitrogen compounds can be met (which is, of course, equally important for Great Britain and all other industrial countries) must be looked for in two directions. One of these, the production of nitrogen compounds from atmospheric air, has been already treated by us (*supra*, pp. 815 *et seq.*). The other is: increasing the output of ammonia in the destructive distillation of coal. No serious increase of this kind can be expected in the manufacture of coal-gas; very much more in that of metallurgical coke. In 1905, Germany produced 35,000 tons of sulphate of ammonia in gas-works (in 1906, 38,000 tons), and 168,000 tons (in 1906, 197,000 tons) from coke-ovens. Assuming that all coke required for the manufacture of pig-iron (in 1905 it was nearly 11,000,000 tons of coke for 16,800,000 tons of pig-iron) was made with recovery of ammonia, the yearly increase in that industry (roundly half a million tons coke), with the methods in use at present, would be 7000 tons of ammonium sulphate = 1470 tons of nitrogen, against the increased demand of 15,000 tons of nitrogen for agricultural purposes, as stated *supra*. The introduction of the recovery of ammonia at all coke-works (in Germany this would yield 230,000 tons of sulphate, against 168,000 tons obtained already in 1905) would afford only temporary relief. Permanent relief must be sought elsewhere, and here Caro turns to the increased production of ammonia from coal by the Mond process. He speaks most

[1] In 1906, the importation of ammonium sulphate into Germany was *nil*.

favourably of this, and states that it has been most successful in practice. In Great Britain about a million tons of coal is worked up by that process, which yields 40 to 50 kg. ammonium sulphate per ton, against 10 to 12 kg. in the coking process. The producer-gas obtained at the same time is certainly of poor quality, 1100 to 1200 cal., but there is a large quantity of it, from 3200 to 3500 cbm. per ton of coal, and is very suitable for evaporating purposes, and particularly, in consequence of its great purity, for the working of gas-engines. This poor gas, which cannot very well be conveyed to great distances, must be utilized on the spot, which has in many cases militated against the introduction of the Mond process, *e.g.*, all over in Germany. But since the spreading of electric central stations, there is a fresh chance for the Mond process for supplying the motive power for these.

In 1908, as stated by N. Caro in a pamphlet, *Die Stickstofffrage in Deutschland*, p. 29, about 1,000,000 tons of coal were treated by that process, and in Germany a company has been formed to introduce it on a very large scale for motor engines. In Staffordshire a whole district is supplied by a Mond plant, consuming 400 tons of coal per day, the gas being conveyed under pressure to the various places of consumption, where it is spent in generating an electric current—thus producing not merely an economic, but also a great hygienic improvement in localities otherwise suffering under the plague of coal-smoke.

The Mond gas-process is also able to tackle the enormous heaps of poor coal waste collecting at the pit-mouths and at the coal-washing stations. That poor coal, containing about 30 to 40 per cent. combustible matter and 60 to 70 per cent. ashes, cannot be burned in grates; it cannot even be taken back directly to the pits, in order to fill out deserted galleries, on account of its large percentage of pyrites, but it has to weather for a year or two. But when used in the Mond process, it yields even more ammonia than corresponds to its real contents of coal, as stated by N. Caro, who obtained by that process from a ton of such "heap coal" 25 to 30 kg. sulphate of ammonia (against 10 to 12 kg. from good coal in the coking process), and 50 to 100 h.p. hours in the shape of electric current.

From a paper by F. G. Rowan, in *The Iron and Coal Trades*

Review, 1908, pp. 1594 *et seq.*, we take the following statements concerning the Mond process. In the earlier practice of this process the producers were worked at "as low a temperature as was compatible with good combustion of the fuel," the air-blast and steam mixed with it being heated only to about 76 C. by means of the air-heating tower before entering the producers. In the later practice the mixture of air and steam is heated beyond that temperature, at least to 150° C., better to 250° C., by means of air-heaters which use some of the sensible heat of the gas issuing from the producers, and by means of a double casing on the producers. It was also found that the treatment of the gases by a sulphuric-acid tower (patented by Neilson in 1882, No. 440, and adopted by Mond), after bringing them into intimate contact with water, materially reduced the value of the tar, at the same time contaminating the sulphate of ammonia and imparting to it a grey colour. Rowan, therefore, holds that the most complete and satisfactory method for the removal from producer-gases of ammonia and tar in good condition, as well as sulphur vapour and vapour of water, is to cool the gases *apart from water* to atmospheric temperature and *then* to wash them with water. The tar is then easily separated from the liquors by gravity, and the NH_3 is separated as gas from the watery solution, and is then combined with uncontaminated sulphuric acid, so that pure sulphate is obtained. By these means Beilby has obtained as much as 134 lb. of ammonia per ton of coal.

Pieper (B. P. 29455, 1896) obtains ammonia from coke by treating it in a continuously working manner by steam in a heated chamber of suitable description.

To this class belongs also the B. P. 8187, 1905, by Aarts.

Wahlen and Caro (B. P. 13668, 1907; Ger. P. 198295) treat the material forming the "waste, or dirt heaps" of collieries, mixed with waste coke from coke-ovens, in an externally heated shaft-furnace through which steam is passed. Combustible gases and porous coke are obtained, and the nitrogen of those materials is converted into ammonia, which may be recovered from the gas. The waste coke used with the coal prevents the material from caking in the furnace. According to a further patent of the same inventors, No. 13669, 1907, they treat the material of those "waste heaps" (which may contain twice as

much nitrogen as corresponds to their contents of pure coal) in a gas-producer by the Mond process, that is to say, with restricted supply of air and with excess of steam, in order to obtain both ammonia and power-gas. The ordinary process, where there is an excess of steam and restricted supply of air, is not available for the dirt heaps, because the materials enter into fusion in that case. The above treatment also destroys most of the pyrites, so that the material cannot spontaneously take fire, and can be employed for filling up disused adits. (The same invention forms the subject of Nikodem Caro's Ger. P. 198205.)

The Mond process can be applied also to a peculiar mass, forming at the bottom of some dried-up lakes in Germany, and called "Schlick" or "Faulschlamm," whose organic substance entirely resembles that of cannel or Boghead coal, and which contains up to 4 per cent. of nitrogen. Caro treats this matter at length in his papers. Its application to the treatment of *peat* has been referred to *supra*, p. 862 *et seq.*

Crossby and Rigby work on similar lines. Their B. P. 24144, of 1906, refers to a former patent, No. 20716, of 1901, according to which the water-vapour and tar are condensed before the ammonia is absorbed, by means of a washer, split up into compartments, in which the washer travels from the cooler to the hotter end, and when heated, is pumped up through an air-tower, by which means it is cooled and can be used over again in the washer, while the air is supplied with steam, and is then used in the producer. The NH_3, going away at the same time, is passed on to an absorbing-tower. According to the new patent, there is some sulphuric acid added to the water, so that a fairly concentrated solution of ammonium sulphate is circulated instead of water, but always containing a certain percentage of free acid to absorb NH_3. Portions of the liquor are taken off as required for further concentration and crystallization in the usual manner.

The *Forty-fourth Annual Report of the Inspectors on Alkali, etc., Works* (for the year 1907) states that a rapid extension of producer plants with recovery of ammonia has taken place in England and Scotland during the past four years. The production of ammonia from this source has risen more than five-fold in this period, that of the United Kingdom tenfold since

1898. Most experts assume that ammonia recovery will not pay for less than 50 tons of coal a day carbonized, but recently an eminent firm of gas-engine makers has adapted it to small producers, gasifying bituminous coal for gas-engine use. It is too soon to speak with confidence as to their success in the hands of ordinary unskilled workmen.

3. Ammonia from Coke-ovens.

Since the recovery of ammonia as a by-product of coke-making is always carried on *pari passu* with that of tar, we have already described this industry in full detail in Chapter II., pp. 57 *et seq.* We have also seen (p. 123) what proportions this industry has already assumed, what quantity of ammonia might be obtained from that source, and that it is just this enormous accession to our sources of ammonia (and tar) which, even at its commencement, is keeping down the prices and rendering the recovery of by-products in coke-making for the present a process of doubtful economy. Still it can hardly be doubted that it is only a question of time when the enormous waste of useful material now going on in coke-making will be a subject of the past, and when it will appear wonderful that it was ever allowed to go on, after it had once been recognized that this need not be the case, and that good coke can be made along with tar and ammonia. Undoubtedly a certain lowering of prices may have to take place; so long as a large quantity of the tar has to be burned as fuel, in which case it may claim to be of decidedly more value than retort-coke, its price can never greatly exceed that of coke; and the price of ammonia will not merely be kept down by the over-production, but also by the competition of nitrate of soda. But fortunately we are not so placed that no reasonable outlet can be found for the products in question; just as there is no limitation to burning tar as fuel, and that at the gas-works themselves, so agriculture is able to take up practically all the ammonia which industry may offer to it, if only the price is low enough. Indeed, in this seems to be the only chance of maintaining a considerably larger population out of the produce of the soil than is done at present. But of course the profits of gas companies on tar and ammonia will inevitably be greatly reduced, and compensation will have to be sought elsewhere.

Concerning the details of condensing-apparatus, we refer to Chapter II.; also to Bolton and Wanklyn's proposal for treating the gases by superheated steam, and then passing them through commercial superphosphate in order to absorb the ammonia (p. 886). We only mention here a patent of P. Frauencron and H. Strack (Ger. P. 32691), according to which hot coke-oven gases are passed through a mixture of coal- or coke-cinders (ashes), as they are produced in metallurgical operations, with coal-duff and lime, and thence passed into the ordinary condensers.

We shall also describe an apparatus patented by Zschokke

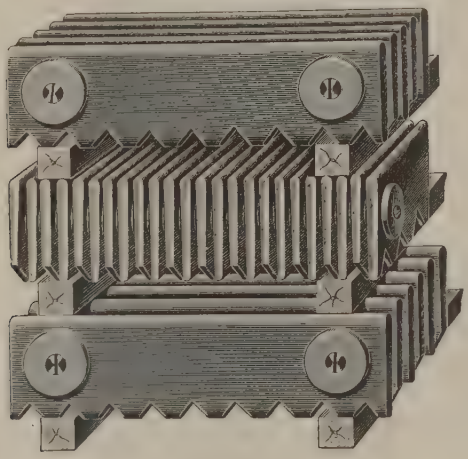


FIG. 223.

especially for a better condensation of ammonia. He constructs wooden shelves (Fig. 223) of flat, rounded staves, conical below, and provided with projections for the drops to fall off. The pressure in the apparatus ought to = zero, and the gas should be very equally divided, as shown in Fig. 224. The free space is about $\frac{1}{3}$ of the total surface, and it is stated that the absorbing surface is 9 to 11 times greater than in the case of the ordinary perforated iron shelves. The water is supplied as shown in Fig. 225. It enters at *a* and is regulated by tap *b*. The lantern *c* allows the formation of the drops to be observed. *z* is a stuffing-box; the wire *h* removes any

obstruction when pushed down. The water falls 3 ft. 3 in. from the tuyere *f* down to the concave plate *d*, and is thus

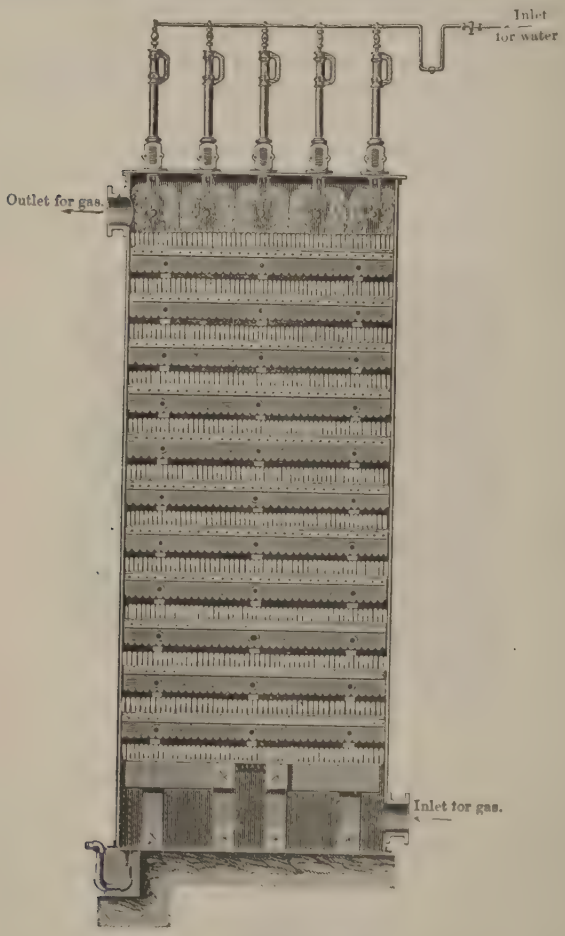


FIG. 224.

converted into a spray, which quite evenly wets the shelves if there is about one such tuyere for each 2 superficial feet. This admits of the supply of water being confined to less than

a gallon per 100 cbm. of gas (3500 cubic ft.), and also of obtaining very strong ammonia liquor. Plate *d* can be removed through door *e* and cleaned.

Fig. 226 shows a plant erected at the coke-works of Messrs Rud. Boecking & Co., near Brebach, and serving for 1,750,000 cub. ft. of gas in 24 hours. By this system only 1 g. NH_3 is left in 100 cbm. gas, against 60 or 80 g. with ordinary perforated plates (patentee's statement).

FIG. 225.

C. Otto & Co., whose coke-ovens with recovery of by-products we have treated at length on pp. 78 *et seq.*, in Ger. P. 171203, of 1906, describe an arrangement intended for a better separation of the products of condensation. By means of a reflux conduit, inclined *towards the receiver*, all products of condensation, not merely tar but also ammoniacal liquor, are conducted back to the receiver, thus producing a mixture of the hot gases coming from the receiver and the backstream of gases, which, on passing the liquids running back, cause a very good cooling and condensation of ammonia and benzol. According to their Ger. P. 174695, the ammoniacal liquor formed in running back, after cooling down, is employed for washing the gases and thus obtaining the volatile ammonia.

Special forms of coke-ovens intended to increase the yield of ammonia in the recovery of by-products are the subject of many more recent patents.

Brunck (B. P. 26253, of 1898) utilizes the combustion air to be fed to the ovens for the condensation of the by-products.

Heinemann (Ger. P. 166380, 1906), in order to get rid of the tar when recovering the ammonia from coke-oven gases, passes these by means of a steam injector into the bath of acid

at such an angle that they blow away the tar and make it run away. Through the injector at the same time enough fresh acid is carried into gas to saturate all the NH_3. The acid tank may also be constructed with a partition over which the blown-away tar flows into a separate compartment.

Brunck (Ger. P. 167022; B. P. 23984, 1904) passes the coke oven gases in a state of fine division through sulphuric acid of sp. gr. 1·7, at such a temperature that the ammonium salts formed separate out in a solid state and can be ladled out, fresh acid being run in as required. The required temperature is produced by the hot gases themselves.

Brunck's Fr. P. 356589 prescribes taking most of the tar out by centrifugallizing the gases before they enter the absorbers.

Reininger (Ger. Ps. 166719 and 167033, 1904) adds to the coke in the ovens calcium carbide, made up into blocks by means of dehydrated tar or other non-aqueous organic agglutinating matter, and during the operation passes nitrogen or gases rich in nitrogen through the oven, in order to increase the yield of ammonia. By Ger. P. 168939 he protects the addition of a mixture of hot dehydrated tar and calcium cyanamide to the coal before coking.

Duff's Fr. P. 352180 treats the gases first in a washer, then in a tower for absorbing the NH_3, and lastly in a cooler. The liquor condensing in the latter is used again in the washer, until it is strong enough to be united with that from the absorbing-tower.

Mars, Buqua, and Laurette (Fr. P. 355375) absorb the NH_3 of the distillation gases by peat or sawdust, impregnated with sulphuric acid, and employ the product obtained directly as a fertilizer.

Andrew Short (*J. Soc. Chem. Ind.*, 1907, pp. 581-585) describes the carbonization of Durham coking-coal and the distribution of nitrogen and sulphur. The higher the temperature, the more ammonia is destroyed and the more cyanide is formed. He finds the liquor to contain 98·31 per cent. nitrogen as ammonia, 1·47 per cent. as cyanides, 0·22 per cent. as sulphocyanides. Of the sulphur, 90·46 per cent. is present as sulphide, 4·96 as sulphocyanide, 3·05 as sulphite and thiosulphate, 1·53 as sulphate.

Dunnachie (Fr. P. 385066, 1907) withdraws the gases from

coke-ovens, gas-producers, etc., from the hottest zone, where cyanogen and cyanides occur. These compounds are directly converted into ammonia by means of steam or atomized water, and if necessary, with a little air.

Lessing (Fr. P. 381186) prevents the gases and vapours, produced between the periods of coke-making, by an arrangement of valves, from entering the main receiver, where they might cause an explosion.

Peters (*J. Gasbeleucht.*, 1908, p. 465) describes the coke-ovens on the regenerative system, constructed by Koppers, and the treatment of the gases therefrom, by which ammonium sulphate is obtained directly. This system has proved thoroughly efficient in a plant treating 100,000 cbm. gas in 24 hours.

C. Otto & Co. (Ger. P. 203254) treat the hot coke-oven gases with a spray of tar or tarry gas-water, produced by a jet of air which at the same time aids in carrying away the gases. Coke-oven gas which before this treatment contained 45 g. of tar in a cubic metre, afterwards showed only 2·5 g., and can be introduced directly into the acid intended for absorbing the ammonia.

Statistics.

The *Forty-fourth Report on Alkali, etc., Works* (for 1907), p. 46, gives the following statistics on the production of ammonia and from coke-ovens, calculated as sulphate, in the United Kingdom. In 1886 the first Semet-Solvay recovery ovens were erected, in 1897 the first Otto-Hilgenstock ovens, and were followed by other types later on. The production in the year 1895 was under 2100 tons. The figures for recent years are:—

	Tons.		Tons.
1898 . . .	5,403	1903 . . .	17,438
1899 . . .	7,839	1904 . . .	20,848
1900 . . .	10,393	1905 . . .	30,732
1901 . . .	12,255	1906 . . .	43,677
1902 . . .	15,352	1907 . . .	53,572

In Germany the increase of this industry is much faster. In the principal coke-producing district, that of Dortmund, the production of sulphate of ammonia from this source increased from 53,636 tons in 1903 to 155,191 tons in 1907.

4. Ammonia from Blast-furnace Gases.

The general principles of the recovery of ammonia, along with a certain description of tar, from blast-furnace gases have been mentioned in Chapter II., pp. 130 *et seq.*; and we must, in the first instance, refer to that description, more especially of the Gartsherrie process (Alexander and M'Cosh's). In this place we only mention those methods which, neglecting the tar, exclusively aim at recovering ammonia from blast-furnace gases.

To begin with, we point out that ammonia can be recovered only from such blast-furnaces as are worked with raw coal, since undoubtedly most of the NH_3 comes from the nitrogen of the coal. But it is certain that some of it is formed from atmospheric nitrogen by reactions taking place within the furnace, principally those which in the first instance lead to the production of cyanides, which are thereupon decomposed by aqueous vapour, but only part of the ammonia thus formed is found in the gases escaping at the furnace mouth, much of it being decomposed again within the furnace.

Hilgenstock in 1885 pointed out that part of the ammonia found in blast-furnace gases should be attributed to the use of certain iron oxides containing water (brown hematites), especially such as have been kept a long time in contact with air.

In England the observation has been made (Hamilton, *Journ. West of Scotland Iron and Steel Institute*, No. 4, 1902; *Stahl. u. Eisen*, 1902, p. 510) that sometimes coals whose quality gives a right to expect a good yield of NH_3 and which show such in the laboratory and at gas-works, give very little NH_3 when employed in blast-furnaces. The reason for this behaviour was sought in the large percentage of water in the ore, which somewhat reduces the temperature, but when this was reduced by partially or entirely roasting the ore, the yield of tar and ammonia did not rise, and the reason of this difference between the behaviour between English and Scotch coals has not yet been found.

Swindells and Lancaster (Fr. P. 115832, of 1876) believe they can recover, not merely the preformed ammonia, but also that obtainable by the decomposition of cyanogen compounds contained in blast-furnace gases, by means of superheated

FIG. 226.

[*To face page* 908.

steam. The gases, after mixing with this, are passed through red-hot fuel, then through milk-of-lime, and finally through red-hot chambers filled with broken bricks, whereupon they are scrubbed for NH_3.

Gavin Chapman (B. P. 5523, 1881) passes the furnace-gases through a chamber in which there is arranged a set of perforated disks. The perforations, through which the gases are made to pass, are alternate, so that the perforation of one disk corresponds to a solid part of the next. The disks are fixed on a horizontal rotating shaft, and their lower parts dip in a vessel containing acid. The lid covering the disks also dips into the liquid, whose evaporating water must be replaced from time to time. Another patent of the same inventor (B. P. 6406, 1884) contains some modifications of this process.

G. Neilson (B. P. 440, 1882) places a very large number of plates, made of earthenware or other material, so as not to be acted upon by acids, with interstices between them, in a chamber, and keeps them sprinkled with a dilute acid, while the gases are passed up between the plates ; the ammonia salts formed drain off at the bottom.

John and James Addie (B. P. 4758, 1882) fix the ammonia in the gases by mixing therewith sulphurous, or sulphuric, or hydrochloric acid in the form of gas or vapour, and subsequently condense and recover the ammoniacal salts formed. Their process has been discussed by A Wilson.[1] It was in the first instance devised in order to avoid the necessity of cooling the enormous amount of gases evolved from a blast-furnace, being thirteen times as much as that coming from a gas-retort for the same quantity of coal. The process has been successfully carried out at the Coatbridge works, and produces sulphate of ammonia of the finest quality. The method is based upon the treatment of the furnace-gases with sulphurous-acid gas, which is allowed to mix with them at any convenient part of the flue along which they pass. The result is the instantaneous formation of sulphite of ammonia, which is carried along by the current of gases. These are then washed in a perpendicular scrubber, the water being kept in circulation by a pump. When this system is applied to the treatment of producer-gas, whose temperature is much higher than that of blast-furnace

[1] *J. Soc. Chem. Ind.*, 1883, p. 458.

gases, the scrubbers must be cooled from the outside by a shower of water. In the case of the treatment of gases not exceeding 260° C., all the water is used inside the scrubbers, and comes out as strong liquor. The specific gravity may be raised up to 40° or 50° Tw., if necessary, by the solution of salts of ammonia. This liquor is then converted into sulphate of ammonia by distillation in the ordinary way; but it may be employed for many purposes as it stands, without conversion into sulphate, such as, for instance, the production of ammonia for the ammonia-soda process or for the manufacture of liquor ammoniæ. The sulphite of ammonia thus obtained is always more or less mixed with sulphate and hyposulphite; but this, of course, is of no consequence, as the distillation with lime brings off the whole of the ammonia. The combination of the ammonia is shown by the following analysis of the crude liquor of 15° Twaddell:—

		Per cent. weight in volume.		
Sulphate of ammonia . .	2·57	containing NH_3		0·66
Sulphite of ammonia . .	3·44	„	„	1·01
Thiosulphate of ammonia . .	4·18	„	„	0·96
Total ammonia salts .	10·19	„	„	2·63

Another crude liquor, evaporated to dryness, gave a salt showing the following composition (Tatlock's analysis):—

Ammonium sulphate . .	36·13 per cent.
„ sulphite . .	19·75 „
„ thiosulphate .	33·10 „
Sodium sulphate . . .	8·58 „
Free sulphuric acid[1] . .	trace.
Insoluble	0·03 „
Organic matter . . .	2·11 „
	100·00[2]
Total ammonia . . .	20·31 per cent.
Equal to sulphate of ammonia	78·85 „

The sulphurous acid used in this process is obtained from sulphurous shale, coal brasses, pyrites, etc., burnt in a retort by means of a forced current of air.

With regard to the question as to whether gas treated in this

[1] How can free sulphuric acid exist in the presence of sulphite and thiosulphate?

[2] *Sic* in the original; the real total is 99·70.

manner carries away any sulphur which might prove objectionable in metallurgical or other processes for which the gas is subsequently employed, it is interesting to quote the following testing (by Dr Clark) of Messrs Addie's gas-flue beyond the scrubbers, the apparatus being worked with excess of sulphurous acid in the ordinary way :—

Sulphur per cubic foot of gas . .	0·1 g.
„ per ton of coal burned . .	1·85 lb.
„ per cent. of coal burned . .	0·08

Hence the sulphur in excess is only about one-tenth of the amount which must exist originally in the coal itself.

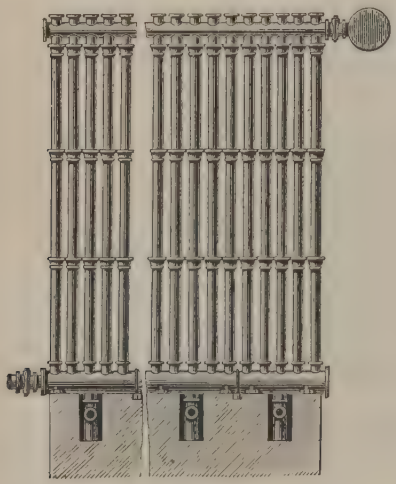


FIG. 227.

FIG. 228.

Instead of sulphurous acid, R. Main and W. Galbraith (B. P. 10448, 1884) bring the gas from blast-furnaces, or that evolved in the destructive distillation of coal, shale, etc., into contact with a spray of hydrochloric acid, and afterwards convert the ammonium chloride into sulphate. This process (already suggested as far back as 1844 by Bunsen and Playfair) has never been carried out in practice, and Addie's process, also known as the Langloan process, *cf.* p. 131, was only worked there from 1884 to 1892. In that year the Langloan furnaces were stopped, and when they were started again in 1900, the Dempster process was introduced.

J. Dempster (B. P. 11250, 1874) places between the blast-furnaces and steam-boilers or or stoves where the furnace-gases are to be burned an ordinary ammonia-still, with its usual sulphate apparatus, "dust-boxes," and "condensers." The gases are then taken to washers and scrubbers, where the last traces of ammonia are absorbed.

Körting Brothers[1] have devised a special arrangement of pipes for cooling and washing the waste gas, as shown in Figs. 227 and 228. The tubes are arranged in three rows; and con-

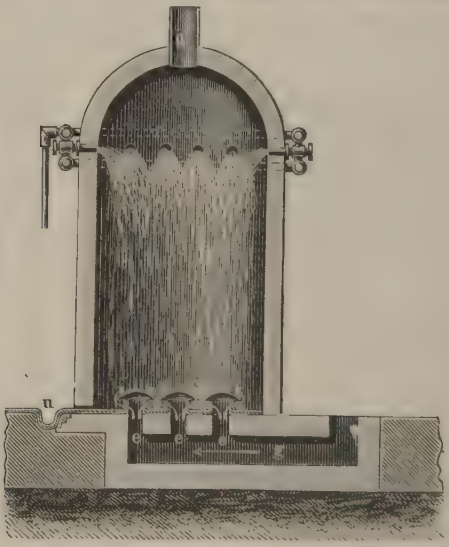


FIG. 229.

nections between the individual pipes of each row are so made that the gases pass up through one set of five pipes and down through the next. A system of 450 tubes, of 1 foot diameter and 12 feet long, gives a total surface of 18,300 superficial feet cooled by the air. An injector may be advantageously applied at different points of such a system.

We shall also show here the washing-chambers, devised by Young and Beilby, intended to decrease the velocity of the stream of gas, and thus to allow a complete separation of tarry

[1] *Dingl. polyt. J.*, ccliv., p. 260; *J. Soc. Chem. Ind.*, 1885, p. 220.

matters (p. 888). In this arrangement (Fig. 229) the gases are introduced by the conduit *g*, and enter the chamber by the openings, *e e*, covered with leaden bells. A fine spray of water, or acid, is maintained during the passage of the gas. The washed gasses pass away by *g*, the washings by *u*.

Fig. 230 shows a somewhat more advantageous arrangement, consisting of a series of chambers built on different levels, so that the liquid employed for washing can be introduced at the opposite end of the system to that at which the gas enters, and passes simply by gravity through the whole series, until spent. Thus it is not necessary to lift the liquid to the top of the

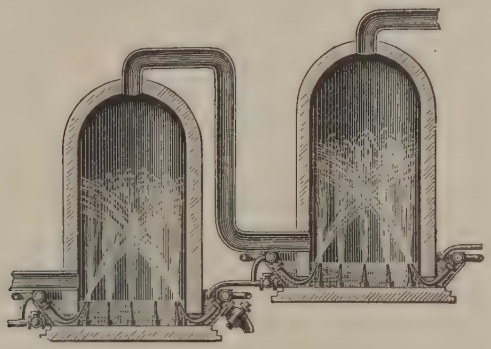


FIG. 230.

chamber and there spray it. The size of the chambers is such that for 100 cubic feet of gas passed through in 24 hours, at least 0·5 cubic foot of space is provided. Large chambers, in which the cooled gases can come to rest and deposit their particles of tar, appear to be most suitable for the complete separation of the tar.

Mackay (B. P. 14060, 1889) scrubs the gases successively with water and tar oil, to extract all the ammonia and tar. He first cools them by passing them in annular jackets round the absorbers. Other patents have been taken out by Imray (B. P. 10589, 1894) and the Coltness Iron Co. (No. 17673, 1889).

At the Summerlee iron-works the gases were, without previous cooling, brought into contact with sulphuric acid in lead-lined towers, thus obtaining a solution of ammonium sulphate. That process was a precursor of the Mond process

(p. 893), but it was abandoned in 1901 and arrangements were made to cool and wash the gases with water, as it is done at all other Scotch iron-works.

R. Hamilton described a process for producing ammonium carbonate from blast-furnace gases, which certainly contain all the CO_2 and H_2O required, but the product never came out sufficiently pure, nor is there a sale for large quantities of that salt.

A paper in the *Transactions of the Institution of Engineers and Shipbuilders in Scotland*, part 25, 1896, states the quantity of ammonia obtainable from blast-furnaces to be about equal to that obtained from coke-ovens. It must, of course, be noticed that only the Scotch splint-coal will give such results, and this is but of local occurrence.

Reininger (Ger. P. 167033) increases the yield of ammonia in blast-furnace work by introducing an alkaline carbide into that part of the furnace where the temperature is about 800 to 1000° C.

According to the *Forty-fourth Report on Alkali, etc., Works* (for 1907), p. 45, iron-works recovering ammonia from blast-furnace gases are almost entirely confined to Scotland, since only in special districts coal is found of sufficient hardness to stand in the blast-furnace without crushing. The English works of this class are confined to Staffordshire. The production of sulphate of ammonia in the United Kingdom was:

1905	. . .	20,376 tons
1906	. . .	21,284 „
1907	. . .	21,024 „

5. Ammonia from Producer-gas.

We have had occasion before to mention the recovery of ammonia from the aqueous fluid condensed from gas-producers or "generators"; thus in connection with the processes of Mond and of Addie (pp. 893 and 909), which Wilson believes to be applicable to his gas-producers. Evidently most of the processes described in the preceding and in the following sections would apply to gas-generators, provided the ammonia produced paid for the cost of the operation, and that the latter did not injure too much the efficiency of the gaseous fuel, which in any case it will do by cooling it.

We may also mention the process of Fogarty (p. 832), although in this the ammonia originally present in producer-gas plays only an insignificant part.

Rigby (B. P. 20716, of 1901) describes a condensing apparatus for that purpose. Schlutius (B. Ps. 2199, 2200, of 1903) treats Dowson gas for this purpose by non-luminous electric discharges in the presence of steam and spongy platinum.

In ordinary cases it does not pay to take the ammonia out of producer-gas, as this contains much less of it than coke-oven gas, and the expense of cooling and washing for a certain yield of ammonia is too great, or even quite prohibitive when anthracite or coke is used, as is altogether the rule for gas-producers. There is no getting over the fact that the temperature at which the producers must be worked to render a good quantity and quality of gas, say from at least 800° up to 1000° C., is deleterious to ammonia, the decomposition of which, when not protected, according to Ramsay and Young, begins at 500° and is fairly complete at 780° C. The presence of a large volume of steam or of hydrogen, etc., retards the decomposition of the ammonia; but in ordinary cases, anyhow, not much of it is found in producer-gas (*cf.* Rowan, *Iron and Steel Trades Review*, 1908, p. 1594).

The case is, of course, different when the recovery of ammonia is purposely made a principal feature, this case has been already treated *sub* No. 2, pp. 888 *et seq.*, especially the Mond process. Clarke, Chapman, & Co. and Robson (B. P. 342A, 1907) combine a gas-producer with an apparatus for driving out the ammonia from the gas-liquor, by surrounding the producer with a jacketed cylindrical heat-interchanger.

Woltereck (*cf. supra*, p. 867), in *Comptes rend.*, 1907, p. 929, discusses the formation of ammonia and cyanides in a Dowson gas-producer.

Lymn (B. P. 8014, of 1908) describes an absorbing-apparatus for the ammonia in producer-gas.

6. Ammonia from ordinary Products of Combustion (Coal-smoke).

We comprise in this section the attempts at recovering ammonia from other sources than those previously enumerated; especially from the products of combustion in ordinary cases, or

where they are mixed with vapours more charged with ammonia, *e.g.*, when carbonizing bones in pot-furnaces. In these cases the methods hitherto enumerated are not sufficient to sift out, as it were, the very small quantity of ammonia from among an enormous volume of diluent gases; nor can it be said that this problem has been satisfactorily solved by any inventor.

Fr. Lorenz (B. P. 6008, 1882) employs the gases from bone-char furnaces first to raise steam, and then passes them through regenerators, to give up most of their heat. After this they are mixed with hot steam; the mixture of gases and steam is sent into a scrubber; the cold gases coming from the scrubber are first reheated, in order to again saturate them with steam, by being made to traverse the regenerators in a direction opposite to that of the gases coming direct from the furnaces, and are then sent into another scrubber fed with dilute sulphuric acid. [The idea of mixing the furnace-gases, containing an exceedingly minute quantity of ammonia, with steam, or water in a fine spray, vaporized by the heat of the gases, in order to make the ammonia more easily condensable in a scrubber, because only in this way would there be a sufficient contact with water for all the dispersed molecules of ammonia, was suggested to the "inventor" in a detailed memoir sent to him by myself (Lunge) on 29th June 1881. This idea has been incorporated in the above patent, without leave being given or any notice received by me.] The German patents Nos. 26638 and 26979 (of 1882) describe the same "invention."

H. Neumeyer (Ger. P. 24511) employs hot sulphuric acid for absorbing ammonia from gaseous mixtures. The acid is converted into a fine spray, by issuing under pressure from holes in a vertical pipe, made of an alloy of lead and antimony, and strikes against the sides of an outer pipe, while the gases containing ammonia travel through the annular space between the pipes. The liquor collecting at the bottom is heated by a steam-coil, and by a force-pump is pumped back into the spray-producer. Thus a hot and concentrated solution is obtained, from which ammonium sulphate separates on cooling.

H. Wellstein (Ger. P. 28762) likewise employs a spray of heated sulphuric acid, which strikes against the cover of the chamber through which the gases containing ammonia are made to travel; whenever a certain quantity of liquor has

collected at the bottom of the chamber, it passes through an automatically opening valve into a pulsometer, where it is subjected to heating from without, and the vapour generated thereby causes the pulsometer to act, and to force the acid liquor back again into the upper reservoir, till it is completely saturated with ammonia.

The Société anonyme Lorraine industrielle de Hussigny (B. P. 5828, 1884) recommends the absorption of ammonia from furnace-gases by calcium chloride. The mixture of calcium carbonate and ammonium chloride formed is either to be used as an ammoniacal manure, or, by heating, sesquicarbonate of ammonia can be obtained, which is to be employed in the ammonia-soda process.

W. Forster (*Chem. Zeit.*, 1894-95) found in the soot from a coal-fire 11·55 per cent. ammonium sulphate. [This seems to be quite an exorbitantly high figure, which cannot be accepted as valid for ordinary purposes.]

Dow (U.S. P. 733465) brings the gases into contact with a hot solution of calcium chloride, adds calcium hydroxide, and blows out the ammonia by a relatively cool gas.

CHAPTER XIII

THE COMPOSITION AND ANALYSIS OF AMMONIACAL LIQUOR, AND PROPERTIES OF ITS CONSTITUENTS

WE have seen in the preceding chapter that, by subjecting gases containing ammonia to a combination of cooling and washing processes, we obtain an aqueous solution of ammonium salts which we call "ammoniacal liquor." We do not in this place include in our enumeration those liquors obtained by the direct action of sulphuric, sulphurous, or hydrochloric acid on such gases, but only those obtained by the action of water alone. The most important source of ammoniacal liquor is the purifying process to which ordinary coal-gas must be submitted, and hence such liquor is commonly called "gas-liquor." The solutions obtained from coke-oven or blast-furnace gases are equally derived from coal, and are quite similar in character to gas-liquor, and they are treated in exactly the same way, so that we shall in the future always include them when considering the former. This would also be the case with liquors obtained from gas-producers, if that method became a working process. Even the liquors obtained from fermented urine, or by the destructive distillation of bones and other animal refuse (pp. 844 and 851), although not identical in composition with those derived from the treatment of coal, are so similar that the same principles are followed in working them up into commercial articles.

Composition of Ammoniacal Liquor.

Ordinary gas-liquor contains the following substances:—

a. *Volatile at ordinary temperatures.*

Ammonium carbonates (mono-, sesqui-, bi-).
Ammonium sulphide, $(NH_4)_2S$.
Ammonium hydrosulphide, $NH_4 . HS$.
Ammonium cyanide.
Ammonium acetate (?).
Free ammonia.[1]

b. *Fixed at ordinary temperatures.*

Ammonium sulphate.
Ammonium sulphite.
Ammonium thiosulphate (hyposulphite).
Ammonium thiocarbonate.
Ammonium chloride.
Ammonium sulphocyanide (thiocyanate).
Ammonium ferrocyanide.

Also the salts of organic bases, especially those of the pyridine series; phenols, and other matters of a tarry or "empyreumatic" character.

The more important of these substances will be described towards the end of this chapter. The term "fixed" in this case is not to be understood in its absolute sense, but in so far as the compounds of ammonia with carbonic and sulphhydric acids can be removed from their solutions by simply exposing them to a sufficiently prolonged boiling, certainly not in the state of unchanged vapours of ammonium salts, but dissociated into less complicated compounds; but the ammoniacal salts, called "fixed," are not removed from their solutions by boiling, or are only very partially decomposed by most prolonged heating of the solutions, so that the ammonia contained in them must be recovered by heating the solutions in the presence of lime, which sets the ammonia free. This is an important distinction in the practical working-up of gas-liquor.

The proportion of the total ammonia to the "fixed" ammonia varies according to circumstances. Fixed ammonia

[1] The presence of free ammonia in gas-liquor is doubted by most chemists, but is asserted by two competent observers, Gerlach and Tieftrunck (*Wagner's Jahresber.*, 1877, p. 1065). It must certainly be formed by hydrolytic action from ammonium salts.

naturally occurs in much larger proportion in the hydraulic main, where the first condensation takes place, than in the condensers and scrubbers; it may amount to more than 50 per cent. of the total ammonia in the former, against 1 or 2 per cent. in the latter. This proportion is, moreover, influenced by the composition of the coal. Thus the percentage of ammonium chloride in the gas-liquor will naturally depend upon the percentage of chlorine in the coal distilled. The percentage of fixed ammonia will also be influenced by the temperature of the gas-retorts, by the temperature to which the gas-liquor has been exposed, by its exposure to the air (which oxidizes sulphide into thiosulphate and perhaps higher than that), and by the general method of washing and scrubbing the gas (J. H. Cox, *J. Gas Lighting*, etc., Report of the Leeds Meeting, 6th Oct. 1883).

The following tables (pp. 921, 922) are constructed from the materials supplied in the just-mentioned paper by Mr Cox; but the thiosulphate is not, as there, included in the "volatile" salts, since experiments made by myself have convinced me that it decomposes on boiling hardly more than the chloride.

According to Wanklyn (*Gas-Engineer's Chemical Manual*), virgin gas-liquor from the first parts of the plant may contain free ammonia, because this is more quickly absorbed than the other constituents, but in passing through the scrubbers enough CO_2 is absorbed to convert all the free ammonia into carbonate. If the same liquor is used over and over again for scrubbing, a good deal of the ammonium sulphide is also converted into carbonate, H_2S being given off.

Detailed analyses of gas-liquor, obtained under different conditions, are given by L. T. Wright.[1]

According to information received from one of the largest German ammonia-works, it is calculated there that liquor from English coals contains from 15 to 20 per cent. of the total ammonia in the "fixed" state, that from Westphalian coals 5 to 10 per cent.; while in liquor from Saxon coal the fixed ammonia may amount to two or three times as much as the volatile.

We will still refer to some recent analyses (by Mr Linder) contained in the *Forty-second Report on Alkali, etc., Works*, for the year 1905, pp. 35, 36. Many other analyses of ammoniacal

[1] Abstracted from the *J. Gas Lighting*, in the *J. Soc. Chem. Ind.*, 1886, p. 655.

I. *Table showing the Properties and Composition of eight samples of Gas-liquor obtained from the same Coal, but taken from different points in the Condensing- and Scrubbing-plant.*

	Condensed in the hydraulic main.	Another point of the hydraulic main.	Liquor from first condenser column.	From second condenser column.	From third condenser column.	From fourth condenser column.	From first washer.	From finishing washer.
Colour	Very dull orange, turned black in air	Ditto.	Colourless	Almost colourless	Brown-red from light tar oils	Dark brown, from tar oils	Colourless	Colourless
Specific gravity in deg. Twaddell at 15°·5 C. . . .	2½	2½	7	15	23	24	4½	2
Ounces by distillation test .	6·1	6·0	16·2	36·1	53·0	58·0	16·5	8·3
Ounces by saturation test .	2·7	2·8	15·9	35·7	52·5	57·4	16·1	8·1
Am. sulphide, grms. per gallon	364	440	2430	5000		8440	1592	1220
=NH_3 „	182	220	1215	2500	7905 NH_3	4220	796	610
Am. carbonate „	564	510	3384	8120		12126	4512	1690
=NH_3 „	200	81	1200	2880		4300	1600	600
Am. thiosulphate „	122	82	Trace	125	352	765	230	135
=NH_3 „	28	19	Trace	41	81	176	51	31
Am. sulphate „	8	34	...	...	...	...	...	...
=NH_3 „	2	9	...	...	...	...	...	...
Am. sulphocyanide „	112	130	91	Trace	...	...	112	27
=NH_3 „	25	29	2	Trace	...	...	25	6
Am. chloride „	1552	1455	119	155	201	107	88	38
=NH_3 „	493	462	38	50	64	34	28	12
Am. ferrocyanide „	...	Trace	22	41	125	375	...	...
=NH_3 „	...	...	5	10	30	90	...	...
Total ammonia, grms. per gal.	930	920	2460	5480	8080	8820	2500	1260
Percentage of fixed ammonia in the total ammonia . .	59 p.c.	56 p.c.	1·8 p.c.	1·85 p.c.	2·2 p.c.	3·4 p.c.	4·2 p.c.	4·0 p.c.
Ammonia expressed as cwt. of sulphate per 1000 gallons .	4·5	4·5	11·9	26·6	39·3	42·8	11·8	6·1
Value of liquor for sulphate-making.	Very small	Very small	Very good	Very good	Excellent	Excellent	Very good	Not quite strong enough

II. *Table showing the Properties and Composition of various samples of Liquor from different Coals and from different points in the Condensing- and Scrubbing-plant.*

	Condensed liquor, passed through scrubber.	Another sample taken at different time.	Same liquor, exposed to air, high temperature.	Hydraulic main liquor.	Part condensed liquor, part hydraulic main.	From "Standard" washer before purifiers.
Colour	Yellow	Yellow	Bright orange	Dull yellow	Yellow	Colourless
Spec. grav. = deg. Tw. at 15°·5	4·5	4	3·5	2	3	4·5
Ounces by distillation test	10·00	8·25	6·90	5·60	6·60	10·00
Ounces by saturation test	8·30	7·00	4·25	3·40	4·90	10·00
Am. sulphide, grms. per gallon	960	1216	630	576	220	1180
$=NH_3$,,	480	608	315	288	110	590
Am. carbonate ,,	2030	1156	800	...	1692	2540
$=NH_3$,,	720	410	283·5	193	600	900
Am. thiosulphate ,,	195	182	236	...	174	Trace
$=NH_3$,,	45	42	52·5	35	40	...
Am. sulphate ,,	...	Trace	39	...	9	...
$=NH_3$,,	...	...	10·5	6	2·5	...
Am. sulphocyanide ,,	338	243	472	...	90	...
$=NH_3$,,	75	54	105	36	20	...
Am. chloride ,,	567	403	891	...	693	32
$=NH_3$,,	180	128	283·5	301	220	10·1
Am. ferrocyanide ,,	Trace	...	...	...	31	...
$=NH_3$,,	...	...	...	...	7·5	...
Total ammonia	1500	1250	1050	860	1000	1500
Percentage of fixed ammonia	20	18·3	43	44	29	0·7
Ammonia expressed as cwt. sulphate per 1000 gallons	7·5	6·00	5·00	4·10	4·85	7·30
Value of liquor for sulphate-making	Not good	Poor	Very poor	Not worth working	...	Very good

TABLE A.

OF GAS-WORKS LIQ

om Storage Wells.)

liquors are given in previous alkali reports, and in the *Forty-fourth Report*, pp. 53 *et seq.*, where especially the proportion of ammonium chloride to fixed ammonia and the cyanogen compounds are dealt with.

From the same report (pp. 46, 47) we take the following tables:—

Distribution of Sulphur in Ammoniacal Liquors from Various Sources.

Liquor (Average).	Per cent. Sulphur to Ammonia.	Sulphur. Per cent. of total.				
		Oxidation Products.				Sulphide.
		Sulphate.	Thiocyanate.	Thiosulphate.	Total.	
Coke-ovens (9 samples) .	27·9	3·2	6·7	6·7	16·6	83·4
Gas-works (6 samples) .	30·4	6·5	29·6	10·0	46·1	53·9
Shale-works (1 sample) .	9·7	4·5	Nil	43·2	47·7	52·3
Iron-works (1 sample) .	2·3	48·9	32·0	19·1	100·0	Nil

Distribution of Cyanogen in Ammoniacal Liquors from Various Sources.

Liquor (Average).	Per cent. cyanogen to ammonia.	Cyanogen. Per cent. of total.			
		Reaction Products.			Hydrocyanic acid.
		Thiocyanate.	Ferrocyanide.	Total.	
Coke-ovens :—					
(1) Virgin (6 samples) . .	3·4	12	3	15	85
(2) Store tanks (11 samples) .	6·1	25	Nil	25	75
Gas-works (9 samples) . . .	8·9	68	7	75	25
Iron-works :—					
(1) Cooler (1 sample) . .	0·8	17	Nil	17	83
(2) Washer (1 sample) . .	0·6	100	Nil	100	Nil
Shale (2 samples)	Nil	...	...	..	...

Ammonium Salts in Recovered Sulphur from Claus-kilns (Gas-works and Coke-oven Liquors).

Sample.	Moisture per cent.	Per 100 parts (undried) calculated as		Hydrocyanic acid in liquor. Grms. HCy per 100 c.c.
		NH_3.	$(NH_4)_2SO_4$.	
GAS-WORKS LIQUOR.				
Works 1.				
First section :— Lumps, dry, crystalline; slightly discoloured. No smell	0·5	0·58	2·25	...
Second section :— Flowers and crystalline lump mixed; moist, discoloured. Smells of SO_2 . . .	6·7	1·72	6·67	...
Third section :— Flowers; wet, pale yellow. Smells of mirbane and SO_2	42·6	0·20	0·78	...
COKE-OVEN LIQUOR.				
Works 2.				
Hot end :— Lumps, crystalline; discoloured and dark in colour .	...	0·54	2·09	0·039
Cold end :— Flowers; dull yellow, moist .	...	2·27	8·81	...

Further analyses of ammoniacal liquors from various sources are given in the *Report*, No. 43, pp. 33 *et seq.*, but the above-quoted analyses will be sufficient for our purposes.

A table showing the variations of the constituents of gas-liquor which occur on keeping it during some time, whereby the sulphide passes over into sulphate, thiosulphate, and sulpho-cyanate, is given by Linder in *J. Gas Lighting*, 1906, p. 642 (*J. Gasbeleucht.*, 1907, p. 1105).

The most recent analyses of gas-liquor, made by the most improved methods, are those given by Mayer and Hempel in *J. Gasbeleucht.*, 1908, pp. 428 *et seq.* They show that the differences between two samples of the mixed liquor, taken in winter and summer, are not very serious, but all the more so those between two samples taken at the same time, one from the hydraulic main and the other from the well containing the

mixed liquor. The volatile compounds in the former are only ⅓ of those in the latter, owing to the high temperature (nearly 100° C.) ruling in the hydraulic main, which causes a considerable dissociation of the volatile compounds. The "fixed" ammonia comes out very similarly in both samples, but that is only apparently the case, the liquor in the hydraulic main being much more concentrated that the mixed liquor in the well. The figures mean grams per litre.

	Well. Jan. 27, 1907.	Well. May 11, 1907.	Hydraulic main. May 11, 1907.
Total ammonia	18·600	17·152	5·794
Ammonia volatile	15·320	14·064	2·916
„ fixed	3·284	3·088	2·880
Ammonium carbonate	40·834	35·260	4·751
„ sulphide	2·803	2·760	0·730
„ thiosulphate	...	1·227	1·427
„ sulphite	...	trace	0·000
„ sulphate	0·295	0·228	0·229
„ chloride	7·404	7·380	7·216
„ sulphocyanide	...	1·820	1·000
„ ferrocyanide	...	0·883	0·119
„ cyanide	...	0·0328	0·035

The following table gives a computation of the amounts of ammonia for the samples taken on 11th May 1907, at the same time from the well and from the hydraulic main. The figures signify grams NH_3 per litre, present in the shape of the salts enumerated:—

	Well.	Hydraulic main.
Total NH_3 found by direct distillation	17·152	5·794
„ as calculated from the sum of the component salts	17·050	4·751
NH_3 present as carbonate	12·5000	1·6850
„ „ sulphide	1·3796	0·3650
„ „ thiosulphate	0·2820	0·0981
„ „ sulphate	0·0588	0·0590
„ „ chloride	2·3500	2·2971
„ „ sulphocyanide	0·4072	0·2240
„ „ ferrocyanide	0·0224	0·0080
„ „ cyanide	0·0464	0·0136

Hence the liquor in the well contains but a very small quantity of free ammonia (0·102 g.), but that in the hydraulic main the considerable amount of 1·043 g. per litre, owing to a

far-going dissociation of the carbonate and sulphide. This free ammonia makes the liquor from the hydraulic main especially fit for the wet purifying process.

Valuation of Ammoniacal Liquor.

This is frequently done at the gas- and tar-works by means of the *hydrometer*, for the sake of convenience. But this process is most deceptive; for the ammonium salts raise the density of the solution in an unequal degree, and free ammonia (which, however, does not frequently occur) lowers it. The following table by Seidel,[1] proves how unequal are the percentages of ammonia in different gas-liquors of the same specific gravity (at 15°).

Degrees Baumé . .	2°	2°·5	3°	3°·5	4°	4°·5	5°	6°
Specific gravity . .	1·0138	1·0163	1·0208	1·0249	1·0280	1·0316	1·0352	1·0426
Per cent. NH_3 . .	1·16	1·30						
	1·42	1·43						
	1·50	1·63	1·63					
	1·77	1·77	1·76					
		1·98	1·90	1·87				
		2·18	2·10	2·00				
		2·65	2·38	2·24				
			2·45	2·40	2·55			
				2·72	2·72	2·79		
					2·90	2·85		
					3·40	3·06		
						3·40		
						3·53	3·67	3·74

Similar observations have been made by T. H. Davis,[2] and the tables on pp. 921 and 922, by Mr Cox, completely bear out the same conclusion. Fischer (*J. f. Gasbel.*, 1909, p. 278) also proves by the examination of 28 samples of gas-liquor that there is no connection between its specific gravity and its percentage of ammonia.

It is consequently decidedly preferable to value gas-liquor by a chemical test. Frequently only the volatile ammonium salts are estimated, the ammonia of which is given off on distillation without lime, and is indicated by titrating with sulphuric acid without heating. The ammonium salts with stronger acids, *i.e.*, the sulphate, chloride, and sulphocyanide,

[1] Hofmann's *Bericht über die Wiener Austellung*, i., p. 194.

[2] *Chem. News*, xxxviii., p. 193.

can be all the more left out of account, as the ammonia thus present hardly ever amounts to more than 0·3 per cent.

The most rational way (which is also the usual one in Germany) is, to employ the ordinary standard acid, which contains 0·049 g. SO_4H_2 per cubic centimetre, and indicates 0·017 g. NH_3. When litmus is employed, a certain volume of gas-liquor, say 20 c.c., should be first supersaturated with standard acid (for which purpose 40 c.c. will suffice in most cases), and boiled to expel all carbon dioxide and hydrogen sulphide; and then the litmus solution is added and the excess of acid retitrated by standard alkali (soda or seminormal ammonia). In *direct titration* with acid a solution of litmus cannot be very well employed, because it is discoloured by sulphuretted hydrogen; in this case litmus-paper can be employed, which, after a little practice, does not take much time; or else some of the azo-colours are employed, which permit exact working in the cold and are not affected either by CO_2, or H_2S, of which the best known is the "methyl-orange." It is the dimethylanilineazobenzenesulphonate of soda, and it is not to be confounded with the "tropæolines," which yield much less precise results.[1]

In England it is usual to state the percentage of gas-liquor in "ounces." This refers to the number of ounces of real sulphuric acid (H_2SO_4) required for saturation by each gallon of gas-liquor, and the test is made as follows:—A standard liquid is prepared by diluting 16½ ounces of real sulphuric monohydrate, H_2SO_4, with water to the volume of a gallon. The specific gravity of the dilute acid ought to be = 1·068, according to the usual statement. This, however, is useless without, at the same time, stating the temperature. At 15° C. an acid containing in 100 parts by volume 10 parts by weight of real H_2SO_4 will have the specific gravity 1·064; it is, of course, much better not to rely upon a specific-gravity test, but to test your standard acid in the usual way, say, with pure sodium carbonate.[2]

The test itself is performed by measuring off 16 liquid

[1] Compare the author's special directions in the *Technical Chemists' Handbook*, p. 242.

[2] This operation is described in every text-book of Analytical Chemistry; also in full detail in Lunge's *Technical Chemists' Handbook*, p. 241.

ounces of the gas-liquor to be examined, and running in the test acid from a measure or burette graduated to liquid ounces, till litmus-paper indicates neutrality. The number of the measures of acid indicates the number of ounces of real sulphuric acid required for each gallon of gas-liquor. It is generally supposed that each degree Twaddell corresponds as nearly as possible to 8 ounces of sulphuric acid; *e.g.*, gas-liquor of 4 Tw. will saturate 8 ounces of acid. This, however, is anything but correct, as is best shown by Cox's table, pp. 921 and 922. It is therefore altogether misleading and objectionable to double the figure found by Twaddell's hydrometer and call this the "ounces" per gallon. This is generally to the advantage of the buyer, for nearly in all cases the Twaddell degrees × 2 read far below the actual value of the liquor in ounces.

The test as just described is called the "*saturation test*"; it indicates none but the "volatile" ammonia. If the test-acid is correctly made to contain 100 g. of H_2SO_4 per litre, each ounce used in the test is equal to 0·3469 ounce of NH_3 per gallon, or 0·217 part NH_3 by weight per 100 parts liquor by volume. Knublauch's "Ammoniakprober" is an instrument intended to be used by non-chemical firemen, etc. (*cf.* also Lubberger, *Z. angew. Chem.*, 1899, p. 109.

Where the gas-liquor is contaminated with a large quantity of pyridine bases, Iltyd Redwood shakes up 100 c.c. of the liquor with 25 c.c. normal caustic-soda solution and 50 c.c. refined petroleum spirit. After the latter, by thorough agitation, has removed the pyridine bases, 10 c.c. of the aqueous liquid is taken out by means of a pipette, and is titrated with standard acid and methyl-orange, taking account of the normal alkali previously added.

Estimation of Total Ammonia.

This is performed both in the case of ammoniacal liquor and in that of commercial ammonium salts, especially the sulphate. For this purpose several methods are employed.

1. *Distillation test.*—The sample of liquor or salt is distilled with caustic soda, lime, magnesia, or baryta, and the vapours are passed either into water, or better, at once into standard

sulphuric acid, the unsaturated acid being afterwards determined by standard alkali (*cf.* conclusion of this chapter). Some prefer lime, baryta, or magnesia to the alkalis, on the (unfounded) assumption that the former are better, not splitting up organic alkaloids, while equally producing ammonia.

I have shown[1] that lime, magnesia, or soda in excess liberate equally well all the ammonia from ammonium chloride (and hence, presumably, all the "fixed" ammonia); but the distillation ought not to last less than three hours, otherwise the ammonia is not totally expelled. Hence, in analyzing pure ammonium salts it is indifferent which of the three fixed bases is employed, and caustic soda, being the simplest and cleanest to use, is preferable to the others. The compound ammonias and other organic bases behave exactly like ammonia; they are liberated under these circumstances by either soda, lime, or magnesia, and there is no advantage to be derived from employing the latter. Lime or soda, on distilling them for three hours with an excess of ammonium chloride, liberate their full equivalent of NH_3; but magnesia, on distilling for 3 to 5 hours, only about 85 per cent. of the theoretical quantity of NH_3, possibly owing to the formation of a basic magnesium chloride difficult to decompose. Hence magnesia must always be employed in excess. For practical purposes it must be considered that the ammonia manufacturer does not treat his liquors with magnesia, but with lime, and that hence the latter indicates the yield to be expected better than the former. Berthelot and André (*Bull. Soc. Chim.*, xlvii., p. 835) have proved that certain ammonium salts are not at all decomposed by magnesia, even on boiling, and only partially by lime, while soda decomposes them entirely.

The distillation test is very conveniently performed in the apparatus shown in Fig. 231. A is a flask, provided with a funnel-pipe closed by a pinchcock, for running in the caustic-soda solution; *b* is the gas-delivery pipe, provided with a bulb and cut off obliquely below, connected with the receiver B. The latter is connected with the safety-tube *c*, dipping into the beaker C, to prevent accidental loss by spurting over of standard acid.

At some works they dispense with the funnel-tube *a*, and

[1] *J. Soc. Chem. Ind.*, 1883, p. 514.

even with the U-tube B, employing an open flask as receiver. The flask A would then hold about 400 c.c.; it is charged with 25 c.c. of gas-liquor, to which is added 50 to 150 c.c. water and about 50 c.c. milk-of-lime; the cork is quickly inserted, and thus the connection made with the receiving-flask, already charged with very dilute standard acid. The liquor in A is gradually heated to boiling, which is continued by a small flame, afterwards increased; it is unnecessary to cool the receiver. The distillation is sometimes interrupted after an hour; but this

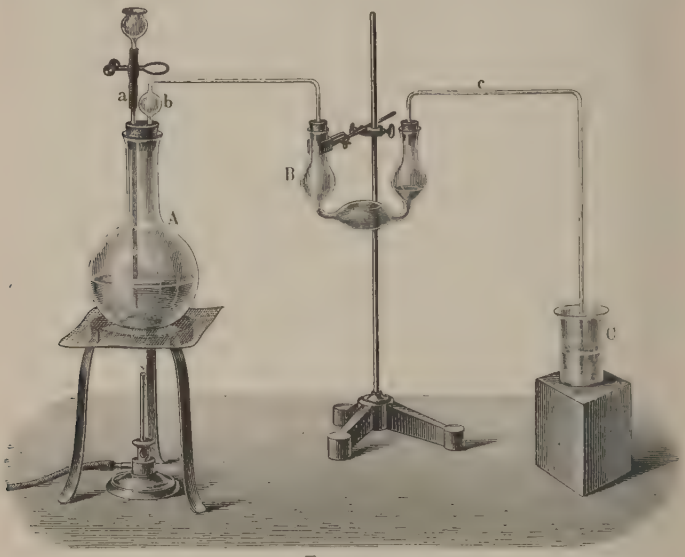


FIG. 231.

does not seem quite enough, and it is better to carry it on for three hours.

In any case we would insist that the analyst convinces himself of the complete expulsion of the ammonia, by suspending, at the close of the distillation, a moistened piece of turmeric or other test-paper in the distillation vessel above the liquid. If this indicates any alkalinity whatever, the test must be repeated.

Stein and Schwarz (*Z. angew. Chem.*, 1889, p. 318) prevent the carrying over of alkali by the arrangement shown in Fig. 232.

The vapours from the flask A pass in B through the lateral holes of the inner tube to the cooler C. The part *f* of the receiver D contains glass beads moistened with standard acid.

Milne (*J. Soc. Chem. Ind.*, vi., p. 423) employs magnesia in the following way:—A 250 c.c. flask is closed by an indiarubber cork through which passes a drop-funnel and a somewhat wide glass tube, leading to a cooler and a receiver charged with standard acid. The flask is charged with the substance to be tested together with 2 g. magnesia and (in the case of salts) 60 c.c. water. It is heated till its contents are nearly dry; then 10 c.c. of water is run through the drop-funnel, the boiling

FIG. 232.

is continued, and this is repeated several times; at last air is aspirated through the apparatus before retitrating the acid.

E. Henry (*Bull. Soc. Chim.* [3], ix., 1018), in the case of gas-liquor containing much sulphide and cyanide, adds a little basic acetate of lime before distillation.

The following details of the process have been found most suitable at the large works of Kunheim & Co., near Berlin. The bulk-sample is well ground up, the whole of it passed through a sieve with about 8 meshes per linear inch, and a small sample taken from it. Of this about 15 g. are weighed, dissolved to 500 c.c.; 50 c.c. of this are introduced without filtering into a 300-c.c. flask and distilled with about 15 c.c.

caustic-soda solution of sp. gr. 1·25 for three hours; the evolved gas is absorbed in 50 c.c. of seminormal standard acid, and titrated back with seminormal soda solution till purple.

Oxalic acid has been frequently recommended as standard acid, but not justly. It is difficult to obtain it perfectly pure, and impossible to make sure that it contains neither too much nor too little water; hence the acid must always be tested in other ways. It is therefore best to employ at once, as cheaper and more stable, sulphuric or hydrochloric acid. The latter is preferable, since its strength can be exactly estimated in two different ways, viz., by titrating a known weight of freshly ignited pure sodium carbonate, and gravimetrically by means of silver nitrate. The standard acid is either made normal, so that 1 c.c. contains 0·049 g. SO_4H_2 or 0·0365 HCl, and indicates 0·017 g. NH_3, or else it is made $\frac{1}{2}$, $\frac{1}{5}$, or $\frac{1}{10}$ of that strength. The standard acid is kept in large bottles protected from great changes of temperature; whenever smaller stock-bottles or the burettes are to be filled with it, the large bottle ought to be shaken in order to mix its contents with any moisture evaporated and again condensed in the empty upper part of the vessel. As standard alkali for retitrating the acid partly saturated by the evolved ammonia, some chemists prefer ammonia or caustic baryta to caustic potash or soda; but ammonia solutions are not sufficiently stable, and baryta solution (which is often used in agricultural laboratories) is much more troublesome to handle than soda or potash.

Far preferable to litmus as an indicator is "methyl-orange" (*cf.* p. 927). In this case oxalic acid is excluded as standard acid; but for retitrating a solution of soda or potash can be employed without any special precautions against attracting carbonic acid, since this does not interfere with the delicacy of the test; and thus titration with caustic potash or soda, with methyl-orange as indicator, is the most convenient of the methods described.

2. *Azotometric test.*—This is founded on the fact that a solution of sodium hypochlorite containing bromine, or of sodium hypobromite, in the presence of a large excess of alkali, almost instantaneously liberates all the nitrogen of ammonia salts. Such a solution is made by dissolving 100 g. of caustic soda in 250 c.c. of water, cooling the liquid (best

by ice), and running in, with constant stirring, 25 g. of bromine. This solution does not keep very long, but decomposes, oxygen being given off.

The azotometer now mostly used is that of Knop, modified by Wagner (Fig. 233). A is the flask for receiving the brominated soda, holding 200 c.c., with an inner tube, *a*, sealed to its

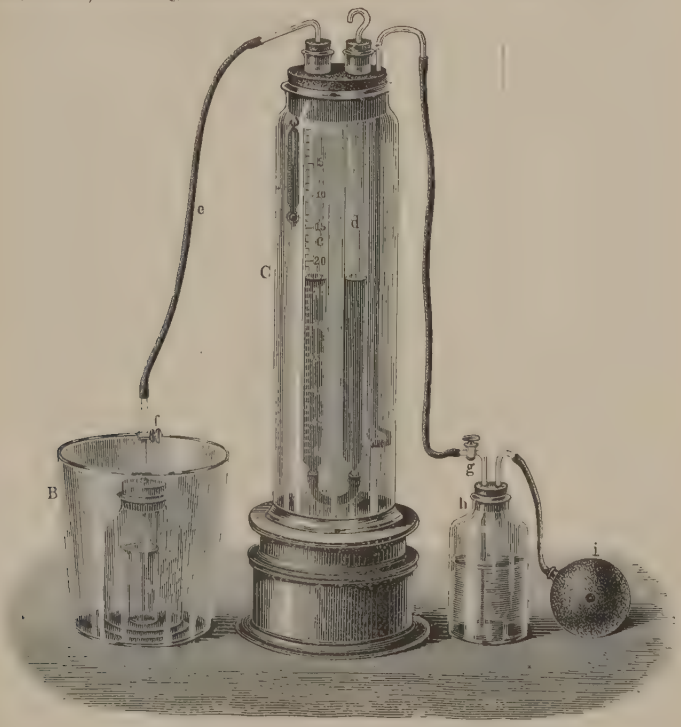


FIG. 233.

bottom. The neck of *a* is ground, to prevent the indiarubber cork from slipping. B is a glass vessel holding about 4 litres of water; C_1 a cylinder filled with water and a little hydrochloric acid (to prevent the growth of fungi), with a wooden lid through which pass the two burettes *c* and *d* and a small thermometer. *h* is a vessel communicating with the burettes by tap *g*, and filled, like these, with coloured water.

To make an analysis, 10 g. ammonium sulphate are dissolved in 500 c.c. water and 10 c.c. of this solution = 0·2 g. of sulphate is introduced into *a*, 50 c.c. of bromine solution are placed in the outer space of A, the cork is put tightly in and the flask placed in the water-vessel B. Tap *f* is slightly loosened, tap *g* is opened, and by compressing the indiarubber ball *i* the burettes *c* and *d* are filled, and by regulating at *g* the level of the liquid is placed at zero. After 10 minutes' waiting, tap *f* is put in tight, but kept open to see whether the level in *c* rises: if it does not rise within 5 minutes, the contents of A have assumed the temperature of the water in B. Now about 30 or 40 c.c. water are run out of *g*, A is taken out and inclined so that some of the ammonia solution mixes with the bromine solution, the flask is shaken, and this is repeated until the liquids are completely mixed and no more gas is evolved. Then A is again placed in B and left for 15 or 20 minutes to assume the temperature of the water-bath. The levels of *c* and *d* are equalized by running water out of *g*, and the volume of gas contained in *c* is read off, together with the temperature of the water in C and the barometric pressure.

The volume of gas read off is reduced to 0 and 760 mm. pressure by the formula:

$$V_1 = \frac{273V(b-f)}{(273+t)760},$$

in which *b* is the barometric pressure (in millimetres), *f* the tension of aqueous vapour at the temperature *t*, *t* the temperature of the water in C. This calculation can be simplified by tables, such as those calculated by myself, by Cl. Winkler, and others. It is also dispensed with by employing, in lieu of the azotometer, the "gas-volumeter" constructed by the author (*cf.* his *Sulphuric Acid and Alkali*, 3rd ed., vol. i., p. 259, or his *Technical Chemists' Handbook*, 1908, p. 217), in which the gas is mechanically reduced to 0° and 760 mm. pressure.

Each cubic centimetre of nitrogen, reduced to normal conditions, corresponds to 0·001254 mg. N or 0·0015246 mg. NH_3. These figures would, however, give a wrong result if used for the azotometric operation without correction, a certain "absorption" of nitrogen taking place, or rather the reaction not being complete.

A correction must be applied on this account, according to

the subjoined table, experimentally determined by E. Dietrich for the case in which 60 c.c. of liquid (50 of brominated soda and 10 of water) are used, of such strength that it is capable of liberating 200 c.c. of nitrogen. This table shows the number of cubic centimetres to be added to the quantity found, when this quantity ranges from 1 to 100 c.c.

Correction for the Volume of Gas found by the Azotometric Method.

Found.	Add.	Found.	Add.	Found.	Add.	Found.	Add.	Found.	Add.
c.c.	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.
1	0·06	21	0·56	41	1·06	61	1·56	81	2·06
2	0·08	22	0·58	42	1·08	62	1·58	82	2·08
3	0·11	23	0·61	43	1·11	63	1·61	83	2·11
4	0·13	24	0·63	44	1·13	64	1·63	84	2·13
5	0·16	25	0·66	45	1·16	65	1·66	85	2·16
6	0·18	26	0·68	46	1·18	66	1·68	86	2·18
7	0·21	27	0·71	47	1·21	67	1·71	87	2·21
8	0·23	28	0·73	48	1·23	68	1·73	88	2·23
9	0·26	29	0·76	49	1·26	69	1·76	89	2·26
10	0·28	30	0·78	50	1·28	70	1·78	90	2·28
11	0·31	31	0·81	51	1·31	71	1·81	91	2·31
12	0·33	32	0·83	52	1·33	72	1·83	92	2·33
13	0·36	33	0·86	53	1·36	73	1·86	93	2·36
14	0·38	34	0·88	54	1·38	74	1·88	94	2·38
15	0·41	35	0·91	55	1·41	75	1·91	95	2·41
16	0·43	36	0·93	56	1·43	76	1·93	96	2·43
17	0·46	37	0·96	57	1·46	77	1·96	97	2·46
18	0·48	38	0·98	58	1·48	78	1·98	98	2·48
19	0·51	39	1·01	59	1·51	79	2·01	99	2·51
20	0·53	40	1·03	60	1·53	80	2·03	100	2·53

Excepting the first few cubic centimetres, this table can be practically dispensed with by putting each cubic centimetre of gas read off = 0·0012818 N or 0·0015582 NH_3.

The azotometric method is more adapted for the estimation of smaller quantities of NH_3 in fertilizers, etc.; for the analyses of commercial sulphate of ammonia the distillation test (p. 928 *et seq.*) is preferable. For raw gas-liquor it is not at all adapted, since the brominated liquor reacts on other organic constituents of this, and thus abnormally high results are produced. (Donati and Pollak, *Z. angew. Chem.*, 1897, p. 555.)

Complete Analysis of Ammoniacal Liquor.

S. Dyson[1] proposes the following methods for a complete

[1] *J. Soc. Chem. Ind.*, 1883, p. 229.

analysis of gas-liquor, taking, however, no account of organic bases and other substances difficult to estimate.

(a) *Determination of Total Ammonia.*—Twenty-five c.c. of the liquor is boiled with magnesia, and the evolved ammonia collected in 50 c.c. standard sulphuric acid, which is afterwards titrated back with standard soda. Suppose this showed 2·045 per cent. NH_3. [Dyson prefers magnesia to lime, because in a check experiment, where he distilled the liquor with lime almost to dryness, 2·152 per cent. NH_3 was obtained, which he, no doubt rightly, attributes to the action of lime on organic substances containing nitrogen. This action of the lime can be easily avoided by employing a more dilute solution, and not boiling to dryness. When employing magnesia, it must not be forgotten that its action is much less energetic and slower than that of lime (*cf.* p. 929).]

(b) *Determination of Total Sulphur.*—Twenty-five c.c. of the liquor are allowed to fall, drop by drop, from a burette into water, acidulated with hydrochloric acid and containing an excess of bromine. The excess of bromine is evaporated off, the solution filtered from the precipitate formed (which seems to consist mainly of tribromophenol), and the sulphur precipitated as barium sulphate. This yields, *e.g.*, 0·3915 per cent. S.

(c) *Determination of Sulphides.*—Zinc sulphate and ammonium chloride are added to 25 c.c. liquor; the precipitate is filtered off and well washed. The filter-paper is perforated, and small portions of the precipitate are gradually washed through into water acidulated with hydrochloric acid, and containing an excess of bromine. When the whole of the precipitate has been washed through, the solution is heated to expel the excess of bromine, filtered, and barium chloride added to the filtrate. Suppose we obtain thus 0·190 per cent. $S = 0·303\ NH_4.HS$.

(d) *Determination of Carbonates.*—An ammoniacal solution of calcium chloride is added to 25 c.c. liquor. The precipitated calcium carbonate is filtered off, dissolved in 50 c.c. standard hydrochloric acid, and the solution titrated back with standard soda. Suppose we thus obtain 1·795 per cent. $CO_2 = 3·916\ (NH_4)_2CO_3$.

(e) *Determination of Chlorides.*—Fifty c.c. are evaporated to dryness on the water-bath. [This might lead to some sal-

ammoniac being volatilized!] Water is added, and the undissolved tarry matters filtered off. The filtrate is mixed with a solution of copper sulphate and ferrous sulphate in about equal proportions (in order to remove thiocyanates) and the liquid again filtered. Nitric acid and silver nitrate are added to the filtrate and the solution is boiled. The precipitate is allowed to settle and the supernatant liquid poured through a filter. Before finally filtering off the silver chloride, it is digested several times with hot nitric acid, to dissolve out the silver sulphide resulting from the decomposition of the silver thiosulphate. [This might easily lead to some AgCl being dissolved! Cf. *infra*, Herting.] The silver chloride is then filtered off and weighed. Suppose we obtain 0·944 Cl = 1423 NH_4Cl.

(f) *Determination of Thiocyanates* (*Sulphocyanide*).—This is not very easy, and is best done in the following way:—Fifty c.c. of the gas-liquor are evaporated to complete dryness, and the residue is heated to 100° for three or four hours, in order to make the precipitate of thiocyanate to be obtained later on less finely divided. The residue is then digested with strong alcohol, rinsed on to a filter, and washed with alcohol. The alcoholic filtrate is evaporated to dryness, water is added, and the insoluble organic matter filtered off. A solution of ammonium thiocyanate is thus obtained tolerably free from other ammoniacal salts (especially thiosulphate) and from organic matter. This solution is precipitated by the addition of cupric sulphate and sulphurous acid (which is preferable to ferrous sulphate as a reducing agent); it is gently warmed (not boiled!) and, after settling, the cuprous thiocyanate, CuCNS, is filtered off. It is then washed into a flask, dissolved in nitric acid, and the liquid boiled for a considerable time. The copper is then precipitated as oxide by caustic soda; the weight of CuO × 0·96 = the equivalent amount of NH_4CNS. Suppose we obtain 0·180 NH_4CNS. [The volumetric method of Liddle and Barnes (*J. Soc. Chem. Ind.*, 1883, p. 122) was found inapplicable to gas-liquor.]

Linder (*Thirty-ninth Alkali Report*, for 1902, p. 229-31) holds that Dyson's method for the estimation of sulphocyanide is not trustworthy.

(g) *Determination of Sulphates.*—Two hundred and fifty c.c.

are evaporated to dryness. Water is added, the organic substances filtered off, and the solution boiled with HCl. A little zinc oxide is added, the liquid filtered, and the sulphates precipitated with barium chloride. Suppose we obtain 0·019 per cent. $(NH_4)_2SO_4$.

(h) *Determination of Thiosulphates.*—This cannot be done by any direct method; but it may be arrived at by subtracting from the amount of total sulphur that existing as sulphides, thiocyanates, and sulphates. In our example:—

Total sulphur		0·3915
Sulphur in sulphides	0·1900	
„ thiocyanates	0·0757	
„ sulphates	0·0046	
	——	0·2703
Sulphur in ammonium thiosulphate		0·1212

$=0·280$ per cent. $(NH_4)_2S_2O_3$.

(i) *Ferrocyanides.*—The residue obtained by evaporating 250 c.c. of the liquor to dryness is dissolved in water, the solution filtered, and ferric chloride added to the filtrate. The precipitate of Prussian blue is filtered off, washed, and decomposed with caustic soda. The ferric hydroxide thus obtained is, after filtering and washing, dissolved in dilute sulphuric acid, reduced, and the solution titrated with centinormal potassium permanganate. The Fe × 5·07 equals the amount of $(NH_4)_4FeCy_6$. Suppose we have found 0·0415 per cent. of this compound.

The result will therefore be that 1 litre of the sample of gas-liquor analyzed contains in grams:—

Total ammonia	20·45		
„ sulphur	3·92		
Ammonium sulphide, NH_4HS . . .	3·03	= 1·01	NH_3.
„ monocarbonate, $(NH_4)_2CO_3$.	39·16	= 13·87	„
„ chloride, NH_4Cl	14·23	= 4·52	„
„ thiocyanate, NH_4CNS . .	1·80	= 0·40	„
„ sulphate, $(NH_4)_2SO_4$ . . .	0·19	= 0·05	„
„ thiosulphate, $(NH_4)_2S_2O_3$ . .	2·80	= 0·64	„
„ ferrocyanide, $(NH_4)_4FeCy_6$.	0·41	= 0·10	„
		20·59	

Herting (*Schilling's J.*, 1900, p. 209) confirms my doubts as to the accuracy of the estimation of chlorine, *supra*, at (c). He

proceeds as follows:—Dilute 10 c.c. gas-liquor to 250 c.c., take out 50 c.c., add a few cubic centimetres nitric acid, decompose by boiling the ammonium sulphide and carbonate, precipitate by an excess of silver nitrate, collect the AgCl, wash it on the filter with hot water, dissolve it on the filter by ammonia (the tarry substances remain behind), acidulate the filtrate with nitric acid, boil up, collect the pure AgCl on a filter, ignite with the usual precautions, and weigh. Titration of the chloride with decinormal silver solution is not feasible, as the potassium chromate indicator does not work in this case.

Cf. also in Chapter XIV. the methods employed for the examination of commercial liquor ammoniæ.

A great many valuable contributions to this chapter have been made by the inspectors under the Alkali Acts, and are recorded in their reports.

In the *Alkali Report*, 1896, p. 23, the remark is made that the estimation of thiosulphates by iodine is difficult in gas-liquor owing to the presence of phenols. It is therefore best to proceed as follows:—Add an excess of zinc sulphate and enough acetic acid to dissolve most of the zinc carbonate. Filter the ZnS, wash with water of 60° or 80°, pierce the filter and wash its contents into an excess of decinormal iodine, adding 2 c.c. concentrated hydrochloric acid, and washing the filter with a little dilute hydrochloric acid. Titrate back with decinormal thiosulphate, and calculate the thiosulphate in the gas-liquor from the difference between the total sulphur and that of the sulphide, sulphate, and sulphocyanide. According to the same source, the estimation of chlorides is performed as follows:—Dilute 10 c.c. gas-liquor, expel the volatile matters by prolonged boiling, dilute to 100 c.c., add 10 c.c. hydrogen peroxide solution, and boil 20 minutes, replacing the water evaporated; add potassium carbonate till the reaction is neutral, boil till the brown-red colour has disappeared, clear up by means of a little sodium bicarbonate, and titrate the cooled liquor with standard silver nitrate.

The *Thirty-sixth Alkali Report*, for 1899, pp. 47 *et seq.*, describes the methods of analysis employed by the chief inspector, Mr R. Forbes Carpenter. These differ from former methods principally as follows:—The thiosulphate is estimated by diluting the filtrate from the mixed zinc sulphide and carbonate, adding a

few drops of strong hydrochloric acid, and titrating forthwith with $N/10$ iodine and starch, taking the *first* appearance of a definite blue colour as the end of the oxidation of thiosulphate to tetrathionate.

The analytical methods employed by Mr Linder (whose tables are given on pp. 920 *et seq.*) are fully described in the *Fortieth Report on Alkali, etc., Works*, for 1903, pp. 31 *et seq.* They may be summarized as follows:—

1. *Ammonia.*—*Free Ammonia* (*a*) by direct titration with $N/2$ sulphuric acid and methyl-orange, to determine approximately the volume of acid required for (*b*). (*b*) Dilute 10 c.c. liquor (more if weak) to 300 c.c. in a round-bottomed flask with catch-bulb, Liebig's condenser and receiver. Distil into a receiver, containing excess of $N/2$ sulphuric acid, provided with outlet acid catch, packed with broken Jena glass. Distil 150 c.c., titrate back the excess of acid in receiver, then distil 100 c.c. into a receiver without acid (the amount of NH_3 in this portion is generally nil).

Fixed Ammonia.—Add boiled caustic soda in excess, with sufficient water to replace that distilled off, and proceed as above.

2. *Carbonic Acid.*—Dilute 10 c.c. to 400 c.c., add 10 c.c. of ammoniacal calcium chloride (1 c.c. = 0·044 g. CO_2), heat in a stoppered bottle for 1½ to 2 hours in a water-bath at 100°, cool, filter, wash, dissolve the $CaCO_3$ in $N/2$ HCl.

3. *Chloride.*—Dilute 10 c.c. of boiled liquor to 150 c.c., add 20 c.c. of hydrogen peroxide free from chloride, boil until the brown colour has almost entirely disappeared, add 10 to 15 drops K_2CrO_4 solution, boil for 5 minutes, cool, neutralize by sodium bicarbonate, and titrate with $N/10$ $AgNO_3$.

4. *Sulphur* (a) *as Sulphate.*—Concentrate 250 c.c. of liquor to about 10 c.c. on the water-bath, add 2 c.c. strong hydrochloric acid, evaporate to dryness to decompose thiosulphate, extract the residue with water, filter, and precipitate the solution with barium chloride.

(b) *As Sulphocyanide* (Thiocyanate).—To 50 c.c. of the boiled solution add ferric chloride in slight excess to precipitate the ferrocyanide as Prussian blue, warm up the solution, filter, cool, add SO_2 solution in sufficient excess, followed by copper sulphate, allow to stand in stoppered flask for 1 to 2 hours,

filter cold, wash the cuprous sulphocyanide thoroughly on the filter, wash it back into the flask, boil with 1 c.c. strong nitric acid until green, cool, add slight excess of sodium carbonate, acidify with acetic acid, add KI, dilute, and titrate the liberated iodine with $N/10$ thiosulphate and starch (details in *Thirty-ninth Alkali Report*, for 1902, pp. 71 to 74).

(c) *As Sulphide, Sulphite, and Thiosulphate.*—(1) Titrate 10 c.c., after dilution to 500 c.c., acidified with HCl, with iodine and starch.

(2) Add 10 c.c. of liquor to excess of ammoniacal zinc chloride solution, filter, wash the ZnS on the filter with warm water, wash it off the filter into excess of $N/10$ iodine, acidified with HCl, and determine the excess iodine with $N/10$ thiosulphate. The sulphite and thiosulphate are found by subtracting the sulphide found as above from the figure obtained in (1).

(d) *Total Sulphur.*—Deliver 50 c.c. drop by drop from a burette into a flask containing excess of bromine, covered by water strongly acidulated with HCl, evaporate to dryness, extract the residue with boiling water, and precipitate the filtrate with barium chloride.[1]

(e) *Polysulphide* cannot exist in ordinary ammoniacal liquors, since it reacts with sulphites and cyanides.

Mayer and Hempel (*J. Gasbeleucht.*, 1908, pp. 381, 403, 425) employ the following methods. *Ammonia*, (a) *volatile*, is estimated by diluting with 10 times the amount of water, distilling and titrating the distillate; (b) *fixed*, by redistilling the residue with caustic alkali or lime; *carbon dioxide*, by adding ammoniacal $CaCl_2$, heating for 2 hours, cooling, filtering, and washing the $CaCO_3$ in a good crucible and titrating; *chloride* and *sulphide*, by Linder's methods (*supra*, p. 940); thiosulphate, by adding an excess of the chlorides of strontium, zinc, and ammonia, washing the precipitate with dilute solution of strontium chloride, acidifying the filtrate and titrating the thiosulphate by means of iodine solution. To determine the *sulphite*, the acidified gas

[1] In *Chem. Tech. Unt. Meth.*, 5th ed., ii., 705, I recommend to acidulate the liquid only slightly, not strongly, to avoid an escape of H_2S. Treadwell (*Anal. Chem.*, 2nd ed., ii., 338) recommends employing as little potassium salts as possible in decomposing the bromine compounds. Mayer and Hempel (*J. Gasbeleucht.*, 1908, p. 425) confirm both these recommendations.

liquor is titrated in the same way, and the sulphide and thiosulphate, obtained as above, are deducted, obtaining the sulphite by difference; *thiocyanate*, by Linder's method (*supra*, p. 940); *sulphate*, by boiling down with hydrochloric acid, extracting the residue with hot water, and precipitating the acidified filtrate with barium chloride; *total sulphur*, as in Dyson and Linder's methods (*supra*, p. 941); *cyanide* and *ferrocyanide*, as below.

Special methods for Sulphides, Cyanides, Phenols, etc.

Walther Feld has published papers on the determination of sulphides, sulphides and thiosulphates (*Chem. Ind.*, 1898, p. 372; *J. Soc. Chem. Ind.*, 1898, p. 1186) and on mixtures containing, in addition to these bodies, sulphocyanide and cyanogen compounds in general (*J. Gasbeleucht.*, xlvi., 1903, pp. 561 and 660; *J. Soc. Chem. Ind.*, 1903, p. 1068). A thorough examination of these methods with unfavourable results was made by Linder (*Forty-first Alkali Report*, for 1904, pp. 27 to 36).

Mayer and Hempel (*J. Gasbeleucht.*, 1908, p. 426) modify Feld's method for estimating the *cyanide* as follows:—They distil 250 c.c. gas-liquor, after adding a sufficient quantity of 20-per-cent. solution of lead nitrate to keep back the H_2S; the distillate is taken up in 25 cbm. standard caustic-soda solution, to which 5 c.c. standard KI solution has been added as indicator. Such a distillation takes about $\frac{1}{2}$ hour.

The same authors declare Feld's method for estimating the *ferrocyanide* to be the only practicable one. They carry it out as follows:—250 (or 500) c.c. gas-liquor are placed in a covered glass dish and are just acidified. Then add a solution of iron-ammonia alum until a permanent red colour has been produced, heat to 60°, allow to cool, filter through a plaited filter, wash two or three times with water containing sodium sulphate, place the filter in a distilling-flask, heat for 5 or 10 minutes with 3 to 5 c.c. of 8-normal caustic-soda solution, add 35 c.c. of 3-normal solution of magnesium chloride, stir up and add to the boiling solution 100 c.c. of a boiling $N/10$ solution of mercuric chloride. After boiling for $\frac{1}{4}$ hour the decomposition is finished, a light brown precipitate has been formed and the liquid is quite clear. Now connect with the cooler and distil the HNC off in the usual manner.

The *phenols* in gas-liquor are determined by Skirrow (*J. Soc.*

Chem. Ind., 1098, p. 58) by a modification of the well-known method of Messinger and Vortmann, viz., distilling them off with water, converting them into tri-iodophenol by means of an excess of iodine and titrating back with thiosulphate In the present case the sulphides and cyanides must be previously removed, and the liquor on evaporation must be permanently and strongly alkaline. One hundred cubic centimetres of the filtered gas-liquor is treated with an excess of ammonium polysulphide, to convert any cyanide present into thiocyanate. The solution is made up to 200 c.c., the sulphides are precipitated by lead carbonate. To 100 c.c. of the filtered solution, 25 c.c. of a 50-per-cent. solution of sodium hydroxide is added and the whole evaporated until the salts begin to separate and the residue is washed into a litre distilling flask and diluted to about 150 c.c. with distilled water, and when cold, acidified with sulphuric acid. The liquid is distilled until the salts begin to crystallize out; we thus obtain "distillate 1." One hundred cubic centimetres is added in the distilling flask, and the liquor again distilled into a second receiver, giving "distillate 2." This is repeated a third time, giving "distillate 3." Each of these distillates is shaken with about 1 g. of calcium carbonate and a little lead carbonate (to get rid of any acid and sulphides carried over), and redistilled. In doing this, No. 1 is distilled first, No. 2 is then added to the flask and distilled, No. 3 being distilled last. The final distillates are united and made up to 500 c.c. One hundred cubic centimetres of this are made alkaline with NaOH, warmed to 60° C., an excess of iodine run in, the flask immediately stoppered and cooled with frequent shaking. Then the solution is acidified and titrated back with $\frac{1}{10}$ normal sodium thiosulphate, starch being used as indicator. About 4 molecules of NaOH to each of phenol should be used in the previous neutralization, to produce a sharp transition from blue to pink, and for this purpose a preliminary test is made, and followed by a final test. The reaction is:—

$$C_6H_5OH + 6I = C_6H_2I_3OH + 3HI.$$

On acidification the excess of iodine, which had passed over into NaIO + NaI, is set free:

$$NaIO + NaI + H_2SO_4 = Na_2SO_4 + H_2O + I_2,$$

and can be titrated.

The author quotes a large number of estimations made in this way, showing generally 0·2 to 0·3 g. phenol per 100 c.c. of gas-liquor, and 0·1 to 0·19 g. in coke-oven liquor. A further examination showed that the phenols in gas-liquor contain about 65 per cent. of pure phenol and 35 per cent. of cresols, etc., owing to the fact that pure phenol has more strongly acid properties than its homologues and is therefore more easily taken up by the ammoniacal liquor. As the quantity of phenols obtained from the coal-tar amounts to about 0·24 kil. per ton of coal, there is nearly as much phenol lost in the gas-liquor, which cannot be expected to be turned to any account.

Pyrocatechine was found by Börnstein (*Ber.*, 1902, p. 4324) in the ethereal extract from the aqueous distillate, obtained by distilling coal at a very low heat.

Pyridine, according to Pinchbeck (*Pharm. J.*, 1909, p. 84; *J. Soc. Chem. Ind.*, 1909, p. 202) is detected as follows in ammoniacal liquor: Dilute 50 c.c. of the liquor, neutralize with HCl, render alkaline with NaOH and shake with 10 c.c. chloroform. To one-half of the chloroform extract add 0·25 c.c. strong hydrochloric acid and 2 drops of a solution of bromine in chloroform. In the presence of a small quantity of pyridine, a crystalline bromo-compound $C_5H_4Br_2$, is precipitated. The other half of the extract is exposed to a current of warm air, the residue left will have the characteristic odour of pyridine, if this be present. For a quantitative estimation, 100 c.c. of the ammoniacal liquor diluted with 100 c.c. water is neutralized with sulphuric acid, rendered alkaline with NaOH, diluted to 400 c.c. and distilled until $\frac{1}{3}$ has passed over. The distillate is treated with 10 g. mercuric chloride, dissolved in 150 c.c. water, the precipitate filtered and washed with cold 92-per-cent. alcohol, which dissolves the pyridine compound with $HgCl_2$. This solution is neutralized, diluted to 400 c.c., and slowly distilled. The distillate should not require for neutralization (indicator: methyl-orange) more than 2 c.c., $\frac{1}{10}$ normal NaOH, equal to 0·00948 per cent. pyridine.

The ammonia in spent oxide, according to J. Carter Bell,[1] is often returned in extremely varying quantity by different chemists, according to the method of analysis employed. He recommends the following method, as being analogous to the

[1] *J. Soc. Chem. Ind.*, 1883, p. 110.

manner in which the oxide can be worked up commercially:— If poor in ammonia, 10 g. are heated in the water-bath till dry. This will give the moisture, and also drive off any volatile ammonia which cannot be profitably collected in practice. The oxide is then washed with boiling water till free from ammonia salts, filtered, and the washings put into a flask. Milk-of-lime is added, and the contents of the flask boiled, and the NH_3 driven over into sulphuric acid. The certificate is made out as ammonia equal to sulphate; for in some cases so much sulphocyanide (thiocyanate) is present as to unfit the salt for manure-making. Bell supposes (but wrongly) that the sulphocyanide is not decomposed by lime, whilst it would be so by soda.[1] If, instead of the solution, the oxide itself were directly boiled with lime or soda, very much nitrogenous matter would be split up and would also yield ammonia, which would falsify the test.

Properties of Ammonia and its technically important Salts.

Ammonia, NH_3.

Colourless gas, of pungent smell and sharp, alkaline taste. Common ammonia, from its admixture of organic bases (pyridine, etc.), has a much more disagreeable smell than pure. Sp. gr. 0·5967; 1 litre at 0° and 0·76 metre pressure, according to the most exact determinations of Guye and Piroza (1908) weighs 0·7708 g. Perman and Davies (*Proc. Roy. Soc.*, May 17, 1906) found practically the same value, viz., 0·77085; the coefficient of expansion between 0° and 20° = 0·003914, between 0° and 100° = 0·003487. Vapour-tension:[2]—

At	− 33°·7	= 1 atmosphere.
„	− 5°	= 4 atmospheres.
„	0°	= 4·8 „
„	+ 10°	= 6·5 „
„	+ 20°	= 8·8 „

[1] I cannot otherwise understand his expression—"Even if the ammoniacal salts are washed out and boiled with strong soda, the results will be too high, owing to the sulphocyanides"—taken in connection with the preceding paragraph, where milk-of-lime is prescribed as the proper way of treating the liquor. But a simple experiment shows that milk-of-lime equally expels the ammonia from ammonium sulphocyanide.

[2] Bunsen, *Pogg. Ann.*, xlvi., p. 95.

By pressure and cold it can be condensed into a mobile, colourless, and strongly refringent liquid of sp. gr. 0·6362 at 0°.

Its boiling-point is mostly put = −32°·5 to 33°·5, but according to E. C. Franklin (*Chem. Centr.*, 1908, i., 209) the value found by Gibbs, viz., −33°·46, is the best. Perman and Davies (*vide supra*) found −33°·5. The specific heat of evaporation at its boiling-point is 341 cal. per gram. At very low temperature liquid ammonia solidifies to a white crystalline mass, melting at −78°·3. Its critical temperature is at 131°.

Composition, 82·39 per cent. N, 17·61 per cent. H; 2 vols. of gaseous NH_3 are formed from 3 vols. of H and 1 vol. of N.

Ammonia cannot be directly burned, but only when mixed with hydrogen. Electricity decomposes it into its elements. The spark of an electric machine acts only slowly and incompletely; better is a wire made red-hot by the electric current, and best of all the sparks from a Ruhmkorff coil (Buff and Hofmann, *Liebig's Ann.*, cxiii., p. 132).

The following table by A. Lange (*Chem. Ind.*, 1898, p. 91), stating the specific gravity of anhydrous liquid ammonia at various temperatures, is of importance, as this substance is now a commercial article and its volume varies considerably with the temperature:—

°C.	Specific gravity.	Relative volume, $V_0=1$.	°C.	Specific gravity.	Relative volume, $V_0=1$.	°C.	Specific gravity.	Relative volume, $V_0=1$.
−50	0·6954	0·9119	5	0·6275	1·0105	60	0·5404	1·1735
−45	0·6895	0·9197	10	0·6207	1·0215	65	0·5310	1·1942
−40	0·6835	0·9277	15	0·6138	1·0330	70	0·5213	1·2162
−35	0·6775	0·9359	20	0·6067	1·0451	75	0·5111	1·2407
−30	0·6715	0·9443	25	0·5993	1·0579	80	0·5004	1·2673
−25	0·6654	0·9529	30	0·5918	1·0715	85	0·4892	1·2963
−20	0·6593	0·9617	35	0·5839	1·0860	90	0·4774	1·3281
−15	0·6532	0·9708	40	0·5756	1·1015	95	0·4652	1·3631
−10	0·6469	0·9802	45	0·5671	1·1180	100	0·4522	1·4021
−5	0·6405	0·9899	50	0·5584	1·1355			
0	0·6341	1·0000	55	0·5495	1·1540			

Ellean & Ennis (*J. Franklin Inst.*, 1898, pp. 145, 189, 280) found the specific heat of liquid ammonia = 1·0206 at 10° C. For other temperatures the formula $0{\cdot}9834+0{\cdot}00365\ t$ must be used.

The following table (from Erdmann's *Anorg. Chem.*, 1906, p. 212) is of great importance for the manufacture of ice, as it

shows the dependance of the degree of cold produced by the evaporation of liquid ammonia from the temperature.

Temperature C.	Pressure, grms. per sq. c.c.	The gas occupies per grm. c.c.	Calories taken up by evaporation, per grm.	Absolute temperature, °C.
−40	720	1607	332·7	233
−30	1190	998	330·6	243
−20	1900	646	327·2	253
−10	2920	432	322·3	263
0	4350	298	316·1	273
+10	6270	211	308·6	283
+20	8790	154	299·9	293
+30	12010	114	289·7	303
+40	16010	87	278·0	313

According to *Amer. Chem. J.*, 1899, pp. 8 *et seq.*, liquid ammonia has a remarkable solvent power for many salts and for dissociating electrolyses.

Decomposition of Ammonia.

Ammonia is decomposed by heat into its elements, but very slowly, especially when mixed with other gases. The conditions of this decomposition have been studied by several chemists, especially by Deville; a more recent examination is by Ramsay and Young (*J. Chem. Soc.*, 1884, vol. xlv., p. 88). We quote their results somewhat in detail, as the manufacture of ammonia and its recovery as a by-product from the coking of coal, from blast-furnaces, etc., is greatly influenced by this instability of ammonia at high temperatures.

The percentages of ammonia decomposed by heat under varying conditions of temperature, material of the vessel, etc., were as follows:—

(1) With a porcelain tube filled with broken pieces of porcelain:

At 500° C.	. . .	1·575	per cent. decomposed.
„ 520°	. . .	2·53	„ „
„ 600°	. . .	18·28	„ „
„ 620°	. . .	25·58	„ „
„ 680°	. . .	35·01	„ „
„ 690°	. . .	47·71	„ „
„ 810° to 830°	. . .	69·50	„ „

(2) With an iron tube filled with broken pieces of porcelain:

At 507° to 527°	. . .	4·15	per cent. decomposed.
„ 600° (current very fast)	.	21·36	„ „
„ 600° (current much slower)	.	34·44	„ „
„ 628°	. . . .	65·43	„ „
„ 676° to 695°	. . .	66·57	„ „
„ 730°	. . . .	93·38	„ „
„ 780°	. . . .	100·00	„ „

(3) With a plain glass combustion-tube lying in the iron tube:

At 780° . . . . 0·24 per cent. decomposed.

(4) With a glass combustion-tube filled with fragments of broken glass tubing:

At 780° . . . . 1·72 per cent. decomposed.

(5) With a glass tube filled with strips of ignited asbestos cardboard:

At 520°	. . . .	2·90	per cent. decomposed.
„ 780°	. . . .	100·00	„ „

(6) With a plain iron tube, no oxide of iron present:

At 780° . . . . 100 per cent. decomposed.

(7) With an iron tube partially oxidized, and therefore water formed:

At 780° . . . . 95 per cent. decomposed.

(8) With a glass tube containing several lengths of iron wire:

At 760° . . . . 75 per cent. decomposed.

(9) With a glass tube containing several lengths of copper wire:

At 760° . . . . 20 per cent. decomposed.

(10) With a glass tube filled with copper reduced from the oxide, to give a large surface:

At 780° . . . . 50·2 per cent. decomposed.

The results may be summed up as follows:—(1) Under the most favourable circumstances (with an iron or porcelain tube, or a glass tube containing asbestos) the temperature at which ammonia-gas begins to decompose lies a little below 500°. (2) In contact with a glass surface, the temperature at which decomposition begins is much higher. (3) The influence of the time of exposure is very great. (4) The nature of the surface of the containing-vessel exerts an enormous influence on the amount of decomposition. (5) The amount of decomposition is greater when the surface is increased. The decomposition was never absolutely complete, just as Deville had found when

decomposing ammonia by the electric spark; probably because N and H recombine to a very slight extent. Such a combination could not be traced by heating a mixture of dry nitrogen and hydrogen; when the gases were moist a trace of ammonia was formed, probably owing to the production of nascent hydrogen from water and red-hot iron.

Theoretical investigations on the reaction:

$$N_2 + 3H_2 \rightleftarrows 2NH_3$$

has been made by Haber and Van Oordt (*Z. anorg. Chem.*, xliv., 341); by Nernst and Jost (*Z. Elektrochem.*, xiii., 521); by Davies (*Z. physik. Chem.*, lxiv., p. 657).

Woltereck (*Comptes rend.*, 1908, 147, 460) finds that ammonia, if purified in the ordinary way, which still contains traces of water and organic impurities, begins to dissociate at 620° and at 650° the gases are explosive. Absolutely dry and pure NH_3 even at 620° shows no trace of dissociation.

Ammonia with red-hot coal gives ammonium cyanide and hydrogen:

$$2NH_3 + C = NH_4.CN + 2H.$$

(This condition is always present in gas-retorts.)

Solutions of alkaline hypobromites expel all the nitrogen from ammonia and its salts. (Upon this fact is based the azotometer, proposed by Knop for estimating ammonia, *supra*, p. 952 *et seq.*) With dry carbon dioxide, dry NH_3 yields ammonium carbamate:

$$2NH_3 + CO_2 = CO\begin{matrix}NH_2\\ ONH_4\end{matrix}$$

If moisture be present, ammonium carbonate is also formed.

Ammonia is absorbed by the chlorides of silver, of calcium, and of zinc, forming compounds which are only decomposed by strong heat. It is absorbed, both from its acqueous solution and that of its salts, by clayey soil, but not by pure kaoline.

Absorption by Water.

Ammonia is absorbed with avidity by water and by alcohol. 1 g. of water at 0° and 0·76 metre pressure absorbs[1] 1146 c.c. of ammonia-gas = 0·899 g. NH_3, at 10° only 0·679 g., at 20° 0·526 g., at 30° 0·403 g., at 100° 0·074 g. (Exact statements as to the influence of pressure and temperature upon the solubility

[1] Roscoe and Dittmar, *Ann. Chem. Pharm.*, cxii., p. 349.

of ammonia in water are given by Roscoe and Dittmar, *loco citato*, and by Sims, *Ann. Chem. Pharm.*, cxviii., p. 345.)

It was formerly assumed that the solutions of ammonia contained a hydrate of ammonium, $NH_4.OH$, analogous to the hydrates of potassium and sodium, etc.; but although the chemical behaviour of liquor ammoniæ altogether favours such an assumption, the thermo-chemical and physical observations of J. Thomson and of D. Tommasi (*Chem. Centr.*, vol. xv., p. 418) disprove the existence of ammonium hydrate.

The former tables of the specific gravities of liquor ammoniæ have been superseded by that of Lunge and Wiernik (*Zeit. angew. Chem.*, 1889, p. 181), which is here subjoined.[1] It refers to a temperature of 15° C.

Spec. grav. at 15° C.	Per cent. NH_3.	1 litre contains grms. NH_3 at 15°	Correction of spec. grav. for ± 1° C.	Spec. grav. at 15° C.	Per cent. NH_3.	1 litre contains grms. NH_3 at 15°	Correction of spec. grav. for ± 1° C.
1·000	0·00	0·0	0·00018	0·940	15·63	146·9	0·00039
0·998	0·45	4·5	0·00018	0·938	16·22	152·1	0·00040
0·996	0·91	9·1	0·00019	0·936	16·82	157·4	0·00041
0·994	1·37	13·6	0·00019	0·934	17·42	162·7	0·00041
0·992	1·84	18·2	0·00020	0·932	18·03	168·1	0·00042
0·990	2·31	22·9	0·00020	0·930	18·64	173·4	0·00042
0·988	2·80	27·7	0·00021	0·928	19·25	178·6	0·00043
0·986	3·30	32·5	0·00021	0·926	19·87	184·2	0·00044
0·984	3·80	37·4	0·00022	0·924	20·49	189·3	0·00045
0·982	4·30	42·2	0·00022	0·922	21·12	194·7	0·00046
0·980	4·80	47·0	0·00023	0·920	21·75	200·1	0·00047
0·978	5·30	51·8	0·00023	0·918	22·39	205·6	0·00048
0·976	5·80	56·6	0·00024	0·916	23·03	210·9	0·00049
0·974	6·30	61·4	0·00024	0·914	23·68	216·3	0·00050
0·972	6·80	66·1	0·00025	0·912	24·33	221·9	0·00051
0·970	7·31	70·9	0·00025	0·910	24·99	227·4	0·00052
0·968	7·82	75·7	0·00026	0·908	25·65	232·9	0·00053
0·966	8·33	80·5	0·00026	0·906	26·31	238·3	0·00054
0·964	8·84	85·2	0·00027	0·904	26·98	243·9	0·00055
0·962	9·35	89·9	0·00028	0·902	27·65	249·4	0·00056
0·960	9·91	95·1	0·00029	0·900	28·33	255·0	0·00057
0·958	10·47	100·3	0·00030	0·898	29·01	260·5	0·00058
0·956	11·03	105·4	0·00031	0·896	29·69	266·0	0·00059
0·954	11·60	110·7	0·00032	0·894	30·37	271·5	0·00060
0·952	12·17	115·9	0·00033	0·892	31·05	277·0	0·00060
0·950	12·74	121·0	0·00034	0·890	31·75	282·6	0·00061
0·948	13·31	126·2	0·00035	0·888	32·50	288·6	0·00062
0·946	13·88	131·3	0·00036	0·886	33·25	294·6	0·00063
0·944	14·46	136·5	0·00037	0·884	34·10	301·4	0·00064
0·942	15·04	141·7	0·00038	0·882	34·95	308·3	0·00065

[1] A new table, by W. C. Ferguson, in *J. Soc. Chem. Ind.*, 1905, p. 787, gives values practically the same as those found by L. and W.

The last of the four columns shows what correction must be made for figures observed at other temperatures than 15° C., in order to reduce them to that standard; but the temperature of observation ought not to be *very much* above or below 15°, since the coefficient of dilatation may differ. If, for instance, at 13° the specific gravity had been found = 0·900, it should be placed lower by 2 × 0·00057, *i.e.* at 0·899, in order to correct it for 15°, which amounts to a difference of $\frac{1}{3}$ per cent. NH_3.

Délépine[1] found the solubility of ammonia in alcohol of various specific gravities as follows:—

Strength of alcohol (per cent.)		100	96	90	80	70	60	50
Temp.								
0°	NH_3 per litre .	130·5	146·0	173·0	206·5	...	246·0	304·5
	Spec. grav. .	0·782	0·783	0·809	0·808	...	0·830	0·835
10°	NH_3 per litre .	108·5	120·0	137·5	167·0	...	198·25	227·0
	Spec. grav. .	0·787	0·803	0·794	0·800	...	0·831	0·850
20°	NH_3 per litre .	75·0	97·5	102·0	119·75	137·5	152·5	182·7
	Spec. grav. .	0·791	0·788	0·705	0·821	0·829	0·842	0·869
30°	NH_3 per litre .	51·5	74·0	77·0	81·75	100·3	129·5	152·0
	Spec. grav. .	0·798	0·791	0·796	0·826	...	0·846	0·883

Ammonia is also copiously soluble in methyl alcohol.

The vapour-pressures of aqueous solutions of ammonia have been examined in great detail by E. P. Perman (*Trans. Chem. Soc.*, vol. lxxix. (1901), p. 718; vol. lxxxiii. (1903), p. 1168). The following is a summary of the values found:—

Temperature.	Per cent. NH_3.	Partial pressure of NH_3.	Partial pressure of H_2O.
0°	9·15	24·8	5·3
0°	19·62	82·5	3·0
19°·9	10·15	80·6	15·1
19°·9	19·40	215·6	12·3
40°	11·06	218·5	49·1
40°	20·85	576·1	37·8
60°	3·86	136·9	144·1
60°	11·31	475·8	130·4

Liquor ammoniæ on electrolysis yields nitrogen and nitrites; in the presence of potassium iodide, bromide and fluoride, also hypobromite, hypoiodite, and nitrogen chloride (Losanowitsch and Iovivitsch).[2]

[1] *J. Pharm. Chim.*, xxv., p. 496; *Fischer's Jahresber.*, 1892, p. 323.

[2] *Z. Elektrochem.*, 1896, p. 246.

Ammonia is an irritant and corrosive agent, both in the shape of gas and of aqueous solution. The former researches of Pettenkofer,[1] Hasselt,[2] and Eulenburg[3] have been superseded by those of K. B. Lehmann.[4] One-twentieth volume per 1000 impart to air a strong smell; 0·3 to 0·35 per 1000 is the strongest dose bearable for half an hour, but it does not act as a real poison, only as an irritant upon the mucous membranes, which can be borne much better by those accustomed to it. Only doses of 2 vols. per 1000 when inhaled for a prolonged time, or doses of 5 vols. per 1000 for a short time, produce a severe and consequently dangerous irritation of the respiratory organs and the mucous membranes of the eye, but only locally, without causing any injury to the other organs or their functions.

The men employed at ammonia-works may contract inflammation of the eyes, stinging headaches, and a peculiar affection of the skin, resulting in eruptions and cracks. The counter poisons are acetic or tartaric acid, diluted with sugar-water; the former may also be employed for inhalation. Hot baths are recommended for promoting the removal of the ammonia through the skin.

Ammonium carbonates.[5]

Several of the compounds of carbonic acid and ammonia formerly assumed to be present are not acknowledged now, and only those mentioned below are recognized. They are all decomposed at 58° to 60° into carbon dioxide, ammonia, and water respectively; hence they do not exist as compounds in the gas while hot, but are only formed on its cooling. According to Hertkorn (*Chem. Zeit.*, 1891, p. 1493), carbon dioxide with aqueous ammonia forms first carbamate, which is converted into carbonate only on boiling (?).

[1] *Sitz.-Ber. bayer. Akad.*, 1887, p. 179.

[2] *Thiergifte und Mineralgifte*, 1862, p. 183.

[3] *Schadliche und giftige Gase*, 1865, p. 190. [4] *Arch. f. Hygiene*, 1886.

[5] An extensive memoir on the combinations of carbonic anhydride with ammonia and water has been published by E. Divers (*J. Chem. Soc.*, 1870, vol. viii., p. 171). The following statements are to a great extent based on that memoir, and are supplemented by private communications, kindly made to the author by Dr Divers, which partly rectify the extracts from Gmelin-Kraut's *Handbook*, given in the first edition of this work.

Neutral salt $(NH_4)_2CO_3,H_2O$ (first described by Divers).—Lengthened plates; smells and tastes like ammonia; deliquesces in the air with formation of acid salt, losing ammonia and water; splits up at 58° into water, carbon dioxide, and ammonia. When it is dissolved in water, it can be recrystallized unchanged by cooling; but the dilute aqueous solution, according to some, already contains a mixture of free ammonia and neutral and acid ammonium carbonate. (This statement is denied by Divers.) The aqueous solution begins to give off gas at 70° or 75°, boils at 75° or 80°, and gives off CO_2 and NH_3 in proportion as they exist in the salt.

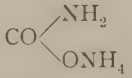
Semiacid salt $(NH_4)_4H_2(CO_3)_3,H_2O$.—Thin hexagonal plates; smell and taste of ammonia. Decomposed by a little water; dissolves unchanged in 5 parts of water at 15°, which solution rapidly evolves gas when heated (Divers).

Acid salt $(NH_4)H(CO_3)$ = ammonium bicarbonate, is found ready formed in many guano-beds, etc., also frequently in gas-purifiers, pipes, etc. This salt is usually assumed to exist in gas-liquor; but some assert that the other carbonates occur there as well. Some of the "commercial" carbonate of ammonia recently manufactured in England is nothing but the bicarbonate, as proved by the analyses of Hanekop (*Arch. Pharm.*, 1886, vol. xxiv., p. 21) and Reissmann (*Pharm. Centralhalle*, 1886, p. 105). It is always formed when the other salts richer in ammonia or ammonium carbamate effloresce. According to Divers, the condition for its formation seems to be the introduction of water-vapour and ammonia in atomic proportions into carbonic anhydride, so slowly that the water is never in sufficient quantity to condense to the liquid state; a warm condenser, therefore, is favourable to it. It occurs as a white mealy powder or as rhombic crystals, mostly columnar. Sp. gr. 1·573 (Schiff); the natural salt = 1·45 (Ulex). In the dry state it does not smell of ammonia; it has a cooling and saline taste. In dry air it is stable; in moist air the crystals lose their brilliancy, decomposition setting in (Berthelot and André, *Bull. Soc. Chim.*, xlvii., p. 848). At 60° it slowly decomposes into CO_2,NH_3, and H_2O. It readily dissolves in water; in the air the solution rapidly loses carbonic acid, and on being gently heated gives off gas-bubbles, a salt richer in ammonia re-

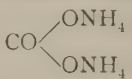
maining behind. According to Dibbits,[1] 100 parts of water dissolve

At 0°	10°	15°	20°	25°	30°	
11·9	15·8	18·3	21·0	23·9	27·0	parts of salt.

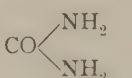
Ammonium carbamate (formerly called dry ammonium carbonate),



is the intermediate term between neutral ammonium carbonate,



and carbamide or urea,



It is always formed when ammonia and carbon dioxide meet nearly in the dry state and not too hot, and even in the presence of moisture if at least 2 vols. NH_3 are present to 1 vol. CO_2; hence it is a principal component of commercial ammonium carbonate, and can be obtained from this by slow distillation, etc. It occurs in prisms or crystalline laminæ or crystalline crusts, smells strongly of ammonia, deliquesces in the air, and almost completely volatilizes.

The vapour-tensions of ammonium carbamate are (in millimetres):[2]—

At 0°, 12·4	At 30°, 124	At 54°·75, 563
„ 10°, 29·8	„ 40°, 248	„ 56°·5, 632
„ 20°, 62·4	„ 47°·25, 361	

The vapours consist of a mixture of NH_3 and CO_2.

At 59° or 60° it decomposes entirely into CO_2 and $2NH_3$; at 50° or 55° it is reformed from these components. It dissolves in 1½ parts of water with considerable absorption of heat, and is then quickly converted into the acid salts, ammonia being given off.

Commercial carbonate of ammonia, salt of hartshorn, sal volatile, is a mixture of ammonium bicarbonate and ammonium carbamate, usually containing a little adhering water. It is

[1] *Dingl. polyt. J.*, ccxvi., p. 164.

[2] Naumann, *Ber.*, 1871, p. 783; Erckmann, *ibid*, 1885, p. 1157.

formed from a mixture of carbon dioxide (even in excess) and ammonia-gas in the presence of sufficient aqueous vapour. According to the opinion once generally entertained, it is also formed in the quick distillation of any of the ammonium carbonates, or of ammonium chloride or sulphate with chalk; but Divers has proved that in this case the neutral carbonate is formed, and this is only converted into the "commercial" carbonate in the process of redistillation (sublimation). Experiments recently made in my own laboratory have entirely confirmed this observation. In all these cases no doubt CO_2NH_3, and H_2O must be assumed to exist free while in the state of vapour. Formerly the commercial salt had the formula

$$2(NH_4)HCO_3, CO(NH_2)(ONH_4),$$
$$= 28.81\ NH_3, 55.96\ CO_2, 15.25\ H_2O;$$

when gently heated in a retort it gradually liquefied, and dissolved

At 13°	16·7°	32°	40°·6	49°	
In 4	3·3	2·7	2·4	2	parts of water.

Divers has proved that the salt analyzed by him (in 1870) was richer in ammonia, according to the formula

$$(NH_4)HCO_3, CO(NH_2)(ONH_4),$$

corresponding to 32·48 NH_3, 56·05 CO_2, and 11·47 H_2O. It remains solid on heating; in the air it effloresces, losing 47 per cent. by weight, and leaving friable ammonium bicarbonate behind (of which the commercial salt now sometimes consists altogether, *cf.* p. 953). The same is left when the salt is treated with a small quantity of water.

It dissolves at 15° in 4 parts of water, with considerable absorption of heat, at 65° in 1½ parts. At 75° the solution begins to give off much CO_2, at 85° also ammonia; at 100° all the salt is volatilized. In dilute solutions the liberation of the salt takes place later on (Divers).

Vogler[1] also considers commercial carbonate of ammonia to be a compound of acid ammonium carbonate with ammonium carbamate. His observations differ from those of Divers only by a direct estimation of the combined water.

According to information received from one of the largest German ammonia manufacturers, two qualities of carbonate of

[1] *Z. anal. Chem.*, xvii., p. 451.

ammonia are found in commerce, one with about 30 per cent. NH_3 (approaching Divers's formula) and the other with about 25 per cent. NH_3. Their value as baking-powders is nearly the same. The acid carbonate (with 21·5 per cent. NH_3) is only occasionally made.

Degrees Twaddell.	Spec. grav. at 15°	Per cent. ammon. carbonate.	Spec. grav. Factor for 1° C.	Degrees Twaddell.	Spec. grav. at 15°	Per cent. ammon. carbonate.	Spec. grav. Factor for 1° C.
1	1·005	1·66	0·0002	16	1·080	23·78	0·0006
2	1·010	3·18	0·0002	17	1·085	25·31	0·0006
3	1·015	4·60	0·0003	18	1·090	26·82	0·0007
4	1·020	6·04	0·0003	19	1·095	28·33	0·0007
5	1·025	7·49	0·0003	20	1·100	29·93	0·0007
6	1·030	8·93	0·0004	21	1·105	31·77	0·0007
7	1·035	10·35	0·0004	22	1·110	33·45	0·0007
8	1·040	11·86	0·0004	23	1·115	35·08	0·0007
9	1·045	13·36	0·0005	24	1·120	36·88	0·0007
10	1·050	14·83	0·0005	25	1·125	38·71	0·0007
11	1·055	16·16	0·0005	26	1·130	40·34	0·0007
12	1·060	17·70	0·0005	27	1·135	42·20	0·0007
13	1·065	19·18	0·0005	28	1·140	44·29	0·0007
14	1·070	20·70	0·0005		1·1414	44·90	0·0007
15	1·075	22·25	0·0006				

The specific gravity of the solutions of commercial ammonium carbonate has been determined by J. H. Smith, with my co-operation.[1] The salt experimented on had the composition—31·3 per cent. NH_3, 56·6 per cent. CO_2, 12·1 per cent. H_2O, which most nearly approaches Divers's formula. The above table shows the specific gravity at 15° and the factor for reducing the specific gravities, found at other temperatures, to 15°.

Suppose we have found a specific gravity of 1·108 at 19°, we shall take that at 15° = 1·108 + 0·0007 (19 − 15) = 1·1108 = 33·71 per cent. ammonium carbonate.

Ammonium Sulphide.

There exist a monosulphide, $(NH_4)_2S$, a sulphhydrate, NH_4SH, and several polysulphides, containing from 3 to 7 atoms of S to 2 molecules of NH_4. They are all volatile, soluble in water, and easily decomposable.

[1] *J. Soc. Chem. Ind.*, 1883, p. 80.

Ammonium Monosulphide, $(NH_4)_2S$, is formed from hydrogen sulphide and ammonia in excess. At $-18°$ colourless shining crystals, dissolving readily and without colour in water. This solution is stable, whilst the crystals in the air at once lose half their ammonia. In the state of vapour it cannot exist, but dissociates in NH_3 and H_2S.

Ammonium Sulphhydrate, NH_4SH, is formed by passing hydrogen sulphide into liquor ammoniæ to saturation (the ordinary laboratory reagent). The originally colourless solution soon turns yellow in the air, polysulphides being formed. Below $-10°$ it can be crystallized; on evaporation it dissociates into H_2S and NH_2. On prolonged contact with air the solution deposits sulphur, and ammonium thiosulphate is formed.

The polysulphides are also prepared by dissolving sulphur in ordinary ammonium sulphide.

Ammonium sulphide has not hitherto been manufactured on a large scale; but this might be done, according to Spence, by mixing in a retort sulphate of ammonia with alkali waste or spent gas-lime (both of them very rich in calcium sulphide), blowing in steam, and passing the vapours into a condensing-apparatus. Care must, however, be taken lest the pipes be stopped up by solidifying ammonium sulphide.

Ammonium Sulphocyanide (*Thiocyanate*), NH_4CNS.

Colourless shining scales, without water of crystallization; the salt crystallized from an aqueous solution is somewhat deliquescent; that from alcohol is stable in the air. Very soluble in water, with considerable lowering of the temperature, and in alcohol. On heating the dry salt it fuses at 245° to 160°, and decomposes soon after. Consequently it cannot exist in the state of vapour, but is only formed on cooling from ammonium sulphide and carbon bisulphide,

$$(NH_4)_2S + CS_2 = NH_4, NCS + 2H_2S,$$

or else from ammonium cyanide and sulphide. In English gas-liquors from 3 to 5 oz. of ammonium sulphocyanide per gallon is found. It is also found in considerable quantities in the spent oxide of iron of the gas-purifiers.

Ammonium Cyanide, NH_4CN.

A colourless salt, crystallizing in cubes, smelling and tasting both of prussic acid and ammonia, with an alkaline reaction, as poisonous as prussic acid. It is very soluble in water and alcohol; it is very volatile, boiling, according to some chemists, at 36°; but, from its vapour-density, it must be assumed to undergo dissociation into ammonia and prussic acid. The dry salt is very unstable, and in the air is quickly converted into a brown nitrogenous substance (azulmic acid).

Carpenter & Linder (*J. Soc. Chem. Ind.*, 1904, 577) estimate the cyanide in ammoniacal liquor by distilling it with an excess of tartaric acid in an apparatus such as serves for ammonia distillation, adding plumbic nitrate and ferrous chloride, and titrate the HCN in the distillate by 1/10 normal silver nitrate or 1/10 normal iodine.

Ammonium Chloride (*Sal-ammoniac*), NH_4Cl.

Known from ancient times; also ready formed in nature, especially in volcanic districts and in the vicinity of coal-fields. In the pure state without colour or taste. Crystallizes from water or alcohol in octahedra arranged in the form of feathers, from urea in cubes. Sublimed sal-ammoniac consists of fritted fibrous crystalline masses. It is very tough and difficult to powder. Sp. gr. 1·52. Soluble in water, with much absorption of heat; 100 parts of water dissolve

At 0°	10°	110°
28·4	32·8	77·2 parts.

Specific gravity of Solutions of Ammonium Chloride at 15°.

Per cent.	Spec. grav.	Per cent.	Spec. grav.	Per cent.	Spec. grav.
1	1·00316	10	1·03081	19	1·05648
2	1·00632	11	1·03370	20	1·05929
3	1·00948	12	1·03658	21	1·06204
4	1·01246	13	1·03947	22	1·06479
5	1·01580	14	1·04325	23	1·06754
6	1·01880	15	1·04524	24	1·07029
7	1·02180	16	1·04804	25	1·07304
8	1·02481	17	1·05086	26	1·07375
9	1·02781	18	1·05367		

Ammonium chloride is not volatile at the ordinary temperature, but is considerably so at the temperature of boiling water.

On being heated further, it evaporates without fusing and sublimes in crusts (as above mentioned). Its vapour is a dissociated mixture of NH_3 and HCl. On boiling its aqueous solution a little ammonia escapes, and the reaction becomes distinctly acid; hence it strongly acts upon metal (especially iron) vessels, and is thereby contaminated. Even in the neutral state ammonium chloride in the presence of water acts strongly upon iron, copper, etc., and promotes the corrosion of these metals.

Ammonium Sulphate.

Of the different sulphates of ammonia we are only interested in the *neutral*, $(NH_4)_2SO_4$, which occurs in transparent rhombic crystals, isomorphous with potassium sulphate. The native ammonium sulphate found in the volcanic regions of South Italy is called *mascagnine*. Sp. gr. 1·76; bitter, acrid taste; decrepitates on being heated, fuses at 140°, and begins to decompose at 280°; it cannot be volatilized without change. One hundred parts of water dissolve at

0°	10°	20°	30°	40°	50°	60°	70°	80°	90°	100°
71·0	73·65	76·3	78·95	81·6	84·25	86·9	89·55	92·2	93·85	97·5

parts of the salt. In absolute alcohol it is insoluble.

Specific gravity of the Solutions of Ammonium Sulphate at 15° C.

Per cent.	Spec. grav.	Per cent.	Spec. grav.	Per cent.	Spec. grav.
1	1·0057	18	1·1035	35	1·2004
2	1·0113	19	1·1092	36	1·2060
3	1·0172	20	1·1149	37	1·2116
4	1·0230	21	1·1207	38	1·2172
5	1·0287	22	1·1265	39	1·2228
6	1·0345	23	1·1323	40	1·2284
7	1·0403	24	1·1381	41	1·2343
8	1·0460	25	1·1439	42	1·2402
9	1·0518	26	1·1496	43	1·2462
10	1·0575	27	1·1554	44	1·2522
11	1·0632	28	1·1612	45	1·2583
12	1·0690	29	1·1670	46	1·2644
13	1·0747	30	1·1724	47	1·2705
14	1·0805	31	1·1780	48	1·2766
15	1·0862	32	1·1836	49	1·2828
16	1·0920	33	1·1892	50	1·2890
17	1·0977	34	1·1948		

Ammonium Sulphites.

A normal, $(NH_4)_2SO_3$, and an acid sulphite, $NH_4.H.SO_3$, are known, neither of which is an article of commerce; but they form an intermediate stage in some processes of the manufacture of sulphate, into which they pass on exposure to the air.

Ammonium Nitrate.

This salt has already been prepared by Glauber and described as *nitrum flammans*. It is obtained by slow evaporation of the aqueous solution in rhombic prisms, or by rapid boiling as a fibrous mass. At the ordinary temperature it is soluble in half its weight of water, at higher temperatures even more easily. The solution takes place with considerable lowering of the temperature; on dissolving 60 parts salt in 100 water of 0° C., the temperature sinks to −16°·7. The salt is also easily soluble in alcohol. On heating, it melts very easily, and on further heating, it is smoothly decomposed into water and laughing-gas: $NH_4NO_3 = 2H_2O + N_2O$. This property is utilized for the manufacture of laughing-gas, much employed as an anæsthetic, especially by dentists.

Nitrate of ammonia deflagrates when thrown on to a red-hot plate. It can also be made to explode by means of mercuric fulminate.[1] It is largely used in the manufacture of explosives.

The specific gravities of solutions of ammonium nitrate at 17°·5 C., according to Gerlach, are:—

Spec. grav.	Per cent.
1·000	0
1·0425	10
1·0860	20
1·1310	30
1·1790	40
1·2300	50
1·2835	60

Solid ammonium nitrate greedily absorbs ammonia, and is thereby liquefied. According to Divers[2] and Raoult,[3] 100 g. absorb at 760 mm. pressure 35 g. NH_3 at 0°, 33 g. at 12°, 21·50 g. at 18°, 23·5 g. at 28°, 20·9 at 29°, 17·5 at 30°·5, 6·0 at 40°·5, 0·50 at 79°.

[1] Lobry de Bruyn, *Z. angew. Chem.*, 1892, p. 499.

[2] *Chem. News*, xxvii., p. 37. [3] *Comptes rend.*, lxxvi., p. 1261.

CHAPTER XIV

THE WORKING-UP OF AMMONIACAL LIQUOR

Storing and Separating from the Tar.

ACCORDING to the nature of things, ammoniacal liquor, such as results from mixing up the aqueous liquids from the hydraulic main, condensers, and scrubbers, is always more or less charged with tarry substances. Some of these are actually dissolved in the water; but others are only present in the state of suspension, and can be separated by proper settling. It is very important that this should be done, as the nuisance caused by working ammoniacal liquor is very much lessened by the removal of these tarry substances.

An excellent arrangement for this purpose is in operation at the Vaugirard gas-works at Paris, where formerly strong complaints were made by the neighbours. It is shown in Figs. 234 and 235, in vertical section and ground-plan. The gas-liquor is stored in large underground brickwork cisterns, GG, and is from these pumped by pumps TT (driven by the steam-engine M) into the four iron tanks B, C, D, E, mounted at a height. These tanks communicate by overflows; the liquor is first pumped into B, and from there gradually runs into C, D, and E. During this passage the settling down of the tar takes place. Most of it is found in B and C, very little in the others. The liquor, now practically free from tar, runs from the surface of the last settler, E, through the pipe S, into the gauging-tank, from which the stills are charged. The tar collecting at the bottom of the first two settlers, B, C, is drawn off by the cock F, and run into iron tank-waggons, to be transported to the tar-works. The small quantity of tar collecting in D and E is run back into the cisterns GG by means of the pipes I, I′, and K.

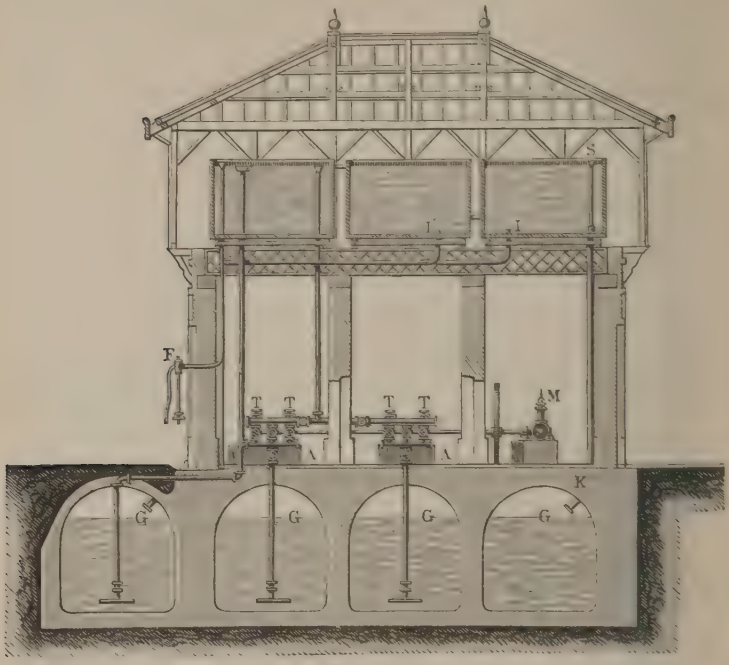


FIG. 234.

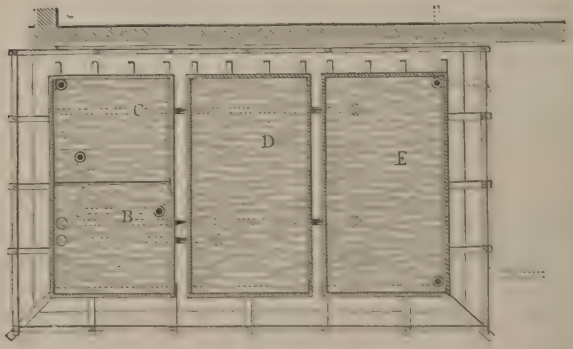


FIG. 235.

The mechanical separation of ammoniacal liquor and tar has been already spoken of in Chapter V., *supra*, p. 315. We here mention another recent process for that object.

The Deutsche Kontinental Gas-Gesellschaft in Dessau (Ger. P. 191342) separates the ammoniacal liquor from the tar by allowing this to flow downwards in an open, inclined spout which passes through the liquor and the tar, contained in a tank, part of the spout being free on the top. Here the ammoniacal liquor, being of less specific gravity, separates from the tar and is at once taken up by the liquor in the tank, when touching it. The tar continues its course downwards in a quiet stream, until it unites with the tar below. For each of these liquids overflows are arranged.

Brunck (B. Ps. 8287, 1903; 15646, 1905; Fr. Ps. 331077 and 356589; U. S. Ps. 824902 and 825297) subjects the gases to centrifugal action, in order to free them from tarry matters, before they enter the absorption apparatus for ammonia.

On a soil liable to changes of level, as is frequently the case near coal-pits, the ammoniacal liquor is preferably stored, not in brickwork tanks, but in iron tanks, set in such manner that they can be inspected and caulked in case of need.

If gas-liquor has to be kept in stock for any length of time it must not be forgotten that it loses a great deal of its ammonia by evaporation. This loss may to a great extent be avoided by running in the fresh liquor near to the bottom of the tank, and pumping it away from the same place. Thus the upper portion of the contents of the tanks remains very nearly unchanged for a long time, and protects the lower portion from a loss of ammonia by evaporation.

A process for *storing ammoniacal liquor* (as well as tar, etc.), in a proper manner is the subject of the Ger. P. No. 204888, of 1906, by Ernst Körting. He forces the liquid with exclusion of air into a tightly closed store-tank, the gas space of which is connected with a coal-gas pipe, in order to prevent rusting of the inside metal, as well as losses by evaporation and nuisance by escaping gases.

Sometimes crude gas-liquor is *directly used as manure;* but its carriage would form an obstacle to a more extended employment of this kind, and the inevitable loss of ammonia by evaporation is also a disadvantage.

Working-up Ammoniacal Liquor without Distillation. Direct Saturation with Acids.

Formerly, the most usual method of treating so much of the gas-liquor as was not run to waste was to *saturate it directly with sulphuric or hydrochloric acid*, and to evaporate the solution till the ammonium salt crystallized out. The gases escaping at the saturation, carbon dioxide and hydrogen sulphide, were sometimes passed through a fire to burn the latter gas, which was done very imperfectly, owing to the admixed moisture and carbon dioxide. The resulting sulphate or chloride of ammonia was very much discoloured by tarry substances, and at the present day would hardly be saleable. Apart from this, direct saturation must be declared irrational, because the evaporation of such dilute solutions takes more fuel than the driving-off of ammonia in properly constructed apparatus; and there is, moreover, a smell of H_2S during the concentration of the liquors. Direct saturation seems to be rarely, if at all, practised now for sulphate, but it is still done for ammonium chloride.

A certain modification of the direct saturation process is practised by Hepworth.[1] The scrubbers are fed with a neutral solution of sulphate of ammonia, which, after having taken up the ammoniacal compounds, is neutralized in leaden vessels with sulphuric acid of sp. gr. 1·7, the escaping gases being passed through an oxide-of-iron purifier. The neutral solution is again pumped up, and this is continued until the strength has risen to 1·20, whereupon the liquor is put into the evaporating-pans. The liquor should never be pumped upon the scrubbers in an acid state, which would cause a loss of illuminating power to the gas.

This process in 1886 yielded 170 tons sulphate from 18,500 tons coal distilled; the gas daily passing through the scrubbers amounted to 800,000 or 900,000 cubic feet.

Treatment with Calcium or Magnesium Sulphate, etc.

The conversion of raw gas-liquor into sulphate is sometimes performed by bringing it in contact with *calcium sulphate* (gypsum); but this yields only a very impure article, and, cheap

[1] *Twenty-third Report on the Alkali Acts*, p. 38.

as this plan seems to be, is not carried out by any large number of works.

Al. MacDougall (B. P. 202, 1882) mixes calcium or magnesium sulphate or chloride with sawdust, bark, peat, or the like, and sprinkles the gas-liquor over it, after having added a little sulphuric or hydrochloric acid. Thus ammonium sulphate or chloride is produced.

De la Martellière (B. P. 2963, 1880) adds to gas-liquor aluminium sulphate, and draws off the resulting solution of ammonium sulphate from the precipitated silica and alumina, which carry down the tarry matters. The purport of this invention is not very clear, since this mode of purification from tarry matters would be rather expensive.

Dubosc & Henzey[1] treat gas-liquor with calcium and ferric chloride, whereby the sulphide is removed, and evaporate the solution of ammonium chloride.

Pfannenschmidt[2] recommends the following process for dealing with gas-liquor at small gas-works, where it does not pay to employ costly apparatus:—The spent oxide of iron is spread out in an open shed in a layer of 6 or 8 inches, and soaked with as much gas-liquor as it will take up. Upon this another such layer is spread, equally soaked with this liquor, and this is several times repeated, the top layer remaining dry. After a few days the heap is turned over till dry, whereupon it will take up more liquor. This must be done in dry, warm weather. The ammonium sulphide first forms iron sulphide, and this is oxidized into ferrous sulphate. This again acts on ammonium carbonate and sulphide, with formation of ammonium sulphate and ferric hydrate, together with iron sulphate, which continues the process. Thus up to 32 per cent. ammonium sulphate can be accumulated in the mass. (No doubt much ammonia will be lost, and a very perceptible smell caused by this process.)

Grahn[3] avoids distilling the gas-liquor by driving out the ammonia by a current of air, and applies heat in case of need. [This process must at all events leave all fixed ammonia behind, and the condensation of the volatile NH_3 salts is thus rendered much more difficult.]

Warth (*Chem. News*, 1906, p. 259), proposes to use plaster

[1] *Bull. Soc. Ind., Rouen*, xvii., p. 439. [2] *J. Gasbeleucht.*, 1884, p. 206.
[3] *Chem. Zeit.*, 1888, rep. p. 169.

of Paris for extracting the ammonia from gas-liquor in places where sulphuric acid is not available in large quantities. By shaking up liquor with plaster of Paris, he recovered 97 per cent. of the ammonia present, viz., 17 per cent., by boiling the solution and absorbing the evolved ammonia in sulphuric acid, and 80 per cent. by concentrating the residual solution to obtain crystallized ammonium sulphate. If it were desirable to dispense altogether with the use of sulphuric acid, the gas-liquor might be first treated with gypsum and the solution drawn off with ferrous sulphate, filtering off the FeS produced.

Kieserite (*native magnesium sulphate*), from Stassfurt, is employed by Kelly and Weigel (B. P. 8680, 1884) in this way:—A mixed solution of kieserite and common salt is cooled down, whereupon sodium sulphate crystallizes out. This is treated by ammonia and carbonic acid; the resulting sodium bicarbonate is separated by filtration, and from the mother-liquor ammonium sulphate is recovered. This is evidently more a process belonging to the domain of alkali-making. This is also the case with Gerlach's process,[1] which is founded upon decomposing concentrated gas-liquor by sodium chloride, sulphate, or nitrate, and passing a stream of carbon dioxide into the liquor, whereupon sodium bicarbonate is precipitated, and ammonium chloride, sulphate, or nitrate remains in solution. This process has never been practically carried out.

Removal of the Cyanides from Gas-liquor before Distillation.

Bower (B. P. 2918, of 1882) converts the cyanide in raw gas-liquor into ferrocyanide before distilling it with lime.

Gutknecht (B. P. 9396, of 1903) also purifies the crude gas-liquor from cyanides and H_2S by addition of ferrous sulphate, so as to make it fit for fresh use. When thus enriched, he treats it with calcium sulphate and recovers the ammonium sulphate thus formed by evaporation. From the iron precipitate he recovers sulphur, ferric oxide, and Prussian blue.

J. Grossmann has worked out a very interesting process for removing the cyanides, for which he has taken out the B. P. 19988, 1907, and upon which he has published a paper in the *J. Soc. Chem. Ind.*, 1908, pp. 393 *et seq.*

[1] *Dingl. polyt. J.*, vol. ccxxiii., p. 82.

The claims of the patent are: (1) The conversion of the cyanide compounds in crude ammonia liquors into ferrocyanide by means of an excess of iron sulphide, carried out with such a quantity of FeS and such an excess of ammonium sulphide as will produce practically only soluble ferrocyanide; (2) The re-use of the iron sulphide from previous in subsequent operations. The inventors who have previously been working at the problem of extracting cyanogen compounds from crude coal-gas have been chiefly trying to obtain insoluble ferrocyanides (which causes complications) or sulphocyanides, the value of which is much less than that of the ferrocyanides. Recently Carpenter and Linder have proved (*Reports on Alkali, etc., Works*) that the crude gas contains cyanogen only as hydrocyanic acid or ammonium cyanide; in the absence of air all the cyanogen in the ammonia liquors is present as ammonium cyanide, and whatever ferrocyanide and sulphocyanide is found, is due to secondary action. The cyanogen may be altogether transformed into these products by suitable treatment, and it is most profitable to aim at the production of soluble ammonium ferrocyanide, on account of its greater value. This might be done by agitation with ferrous oxide or carbonate, but this causes certain drawbacks, especially a loss in the shape of insoluble double compounds. This is avoided by employing ferrous sulphide in the presence of a sufficient excess of ammonium sulphide. The ferrous sulphide must be employed at first in great excess, since the quantity of cyanogen compounds in ammonia liquors varies considerably, but the FeS not converted into ferrocyanide remains behind in an insoluble form and is turned to use in the next operation, where there is a sufficient excess of ammonium sulphide. The iron removed in the shape of ferrocyanide is replaced by ferrous chloride, which is more convenient to add than ferrous sulphide, and which is at once converted into FeS by the NH_4S.

It is best to work continuously in a properly constructed washer, to regulate the addition of ferrous sulphide and chloride so as to ensure the proper quantity of iron compounds being at all times present, to collect the settlings in a store tank, and to determine by tests the quantity required for the conversion of the ammonium cyanide in the next batch of ammonia liquor. The crude liquor should be used as fresh as possible, but it should

be well settled and free from tar. After treatment as above and settling again, it is passed through the ammonia-still in the same manner as at present. The effluent from the still will contain more ferrocyanide and less sulphocyanide than hitherto. It is settled in the usual way and the ferrocyanide is precipitated by ferrous or ferric chloride, in the shape of Prussian blue, which can be easily converted into marketable sodium ferrocyanide. The effluent still remaining should be dealt with as described in a later section of this chapter.

Grossmann points out that, according to Carpenter's and Linder's investigations, in the distillation of crude ammonia liquors, hydrocyanic acid is evolved, and therefore the vapours and condensation products are highly poisonous. This would be completely remedied by the conversion of ammonium cyanide into ferrocyanide. The average quantity of sodium ferrocyanide obtainable per ton of coal carbonized amounts in coke-ovens to about 1·1 lb. and in gas-works to about 1·6 lb. The cost of chemicals and working expenses is about 1 penny per lb. of ferrocyanide, leaving a clear margin of about 2¾d. per ton of coal in coke-works, and over 4d. per ton of coal in gas-works.

Manufacture of Ammoniacal Compounds by distilling the Liquor.

General Remarks.

Question of Boiling with or without Lime (volatile and fixed Ammonia).

Much of the ammonia in ammoniacal-liquor (in good liquor most of it) is present in the form of salts which volatilize on boiling, although with dissociation—essentially ammonium carbonate and sulphide. This "volatile" ammonia can be expelled by simple prolonged boiling of the liquor; but the "fixed" ammonia—that is, that present as sulphate, chloride, sulphocyanide, etc.—remains behind, and can only be expelled by *decomposing the salts with lime.*

We have seen (pp. 919 *et seq.*) that the proportion between "volatile" and "fixed" ammonia varies greatly. In very good liquors only a small percentage of the ammonia is "fixed"; and in such cases the treatment with lime, which complicates the

apparatus and process and greatly prolongs the boiling, does not seem to pay. Hence many (especially English) manufacturers never use any lime in their ammonia-stills (according to *Dr Ballard's Report*, p. 129, only a minority even among English ammonia-makers).

The use of lime, however, ought never to be omitted if the "fixed" ammonia exceeds a very few per cent. of the total ammonia. Although even by the lime treatment the latter is rarely absolutely set free and utilized, yet the additional ammonia gained by its use pays very well for the process if it amounts to at least something like 5 per cent.; and this is probably the general case with gas-liquors mixed from all parts of the condensing- and scrubbing-plant.

J. H. Cox (*cf.* p. 920) considers it a good rule to add 50 lb. of lime per 1000 galls. for every 100 grains of fixed ammonia per gallon of the liquor, that is, 350 lime to 100 fixed ammonia. In practice it is easy, by analyzing the products of manufacture, to arrive at the proper quantity of lime to add, which, of course, is always greatly in excess of the theoretical.

In an apparatus consisting of two stills (in the second of which lime was used), J. Hepworth (*J. Gas Lighting*, October 1883) found the following strengths of liquor:—

As run into No. 1 still . . .	2·540 per cent. NH_3.
„ „ No. 2 still . . .	0·589 „ „
As taken from No. 2 still . .	0·068 „ „

The difference between the two latter tests represents the "fixed" ammonia recovered by lime.

According to the general experience of German gas-works, the fixed ammonia on an average amounts to one-fifth of the total ammonia.

In any case, all apparatus are so contrived that first the volatile ammonium salts are expelled by heat alone, before lime is added to decompose the fixed salts—at any rate, when the production of sulphate is aimed at. Since in all practical cases an excess of lime must be employed, there is always some trouble from *crusts* of calcium hydrate, and even of calcium salts, firmly adhering to the bottom and sides of the still. This is especially awkward in the case of stills heated by direct fire, and is probably the principal cause why so many sulphate

manufacturers forego the recovery of the fixed ammonia; but that drawback may be said to have been entirely overcome by the stills of Grüneberg, Feldmann, P. Mallet, and other modern inventions to be described later on.

It is generally assumed that when an ammonium salt (say ammonium chloride) and calcium hydrate meet, ammonia is immediately set free and calcium chloride is formed. This is contradicted by Isambert,[1] who argues that the reaction

$$2HN_4Cl + CaO = CaCl_2 + 2NH_3 + H_2O$$

absorbs heat to the amount of 10·9 calories; if the lime is used in the caustic state, 7·55 calories should be deducted for the previous formation of $Ca(OH)_2$. Hence at "ordinary" temperatures no ammonia is set free, even *in vacuo;* but the compound $CaCl_2(NH_3)_2$ is produced, in the formation of which 14 calories are evolved, and which gives off its ammonia at 180° to 200°. This is also the case with baryta and strontia, but not with lead oxide.

Without entering upon a discussion as to the validity of these theoretical considerations, it must be stated that a considerable amount of boiling is certainly necessary to expel all the ammonia from the above mixture, that this can be done only by prolonged treatment in the hot state (p. 929), and that it is much better effected in dilute than in concentrated liquors. Usually the treatment in practical working is not continued up to the point where all ammonia is expelled. Cox (*cf.* p. 920) states that at the works he managed the liquor contained 15 per cent. of its total ammonia combined as fixed salt, and that by the lime treatment 5 per cent. of this was recovered, 10 per cent. going to waste; but this is decidedly far more than need be lost. At the same meeting, Hepworth quoted his own case, in which, of the total ammonia, 76·9 per cent. was expelled by boiling alone, 20·5 by treatment with lime, and only 2·6 remained in the waste liquor; and even this (apparent) final loss would probably in reality be less, as caustic soda had been employed for testing, by which some of the cyanides were decomposed. At most German works, also, the loss of ammonia in the waste liquors is quite insignificant. The best proof that Mr Cox's figures do not represent by far the ordinary state of the

[1] *Comptes rend.*, vol. c., p. 857.

case is afforded by the daily practice of all ammonia-soda works, whose ammonia is mostly "fixed," and which could not economically exist if they lost anything like that amount of NH_3 in their waste liquors.

Sometimes the distillation with lime causes a very awkward frothing. This, according, to the Société anonyme des produits chimiques du Sud-Ouest (Ger. P. 18773), is caused by calcium carbonate in a state of suspension. It is therefore proposed by that firm first to drive off the volatile ammonia, and then slightly to acidulate the liquor before adding lime.

Spencer and Sisson (B. P. 92, 1893) slake the lime with hot waste-liquor from the stills, in order to economize heat, to save the lime present in the liquor, and to diminish its volume.

Preparation of the Milk-of-Lime.

The slaking of the lime and the conversion of the slaked lime into a milk are generally known operations. Where it is to be done on a very large scale, the apparatus used for preparing the very large quantities of milk-of-lime required for the Weldon manganese recovery process may be used. This is shown in Figs. 236 and 237. Two cylindrical iron tanks, I and K, are placed one above the other. They are generally about 6 to 8 feet wide, and of the same height. I serves for slaking the lime and preparing the milk, K for storing the latter as a reservoir for the pump. A donkey-engine, *a*, bolted to I, drives the agitating-gear for both cylinders. In I there is a cage, *b*, formed of perforated metal plates, into which the quicklime is put; it occupies a segment of an annular space in the upper third of I, one-third or half round its circumference; the upper cross-arm of the agitator is accordingly shortened. The milk-of-lime runs from I through tap *c* on to the perforated zinc plate in the sieve *d*, and from this into K.

A steam pump, by means of which the exact quantities of milk-of-lime required for liberating the ammonia is supplied to the still in small quantities and in regular intervals, has been patented by the Berlin-Anhaltische Maschinenbau-Aktien-Gesellschaft, Ger. P. 124134.

Hartmann (Ger. P. 164723) also describes a pump for both agitating and pumping the milk-of-lime for ammonia-stills.

C. Menzel Söhne (Ger. P. 165098) describe an apparatus for

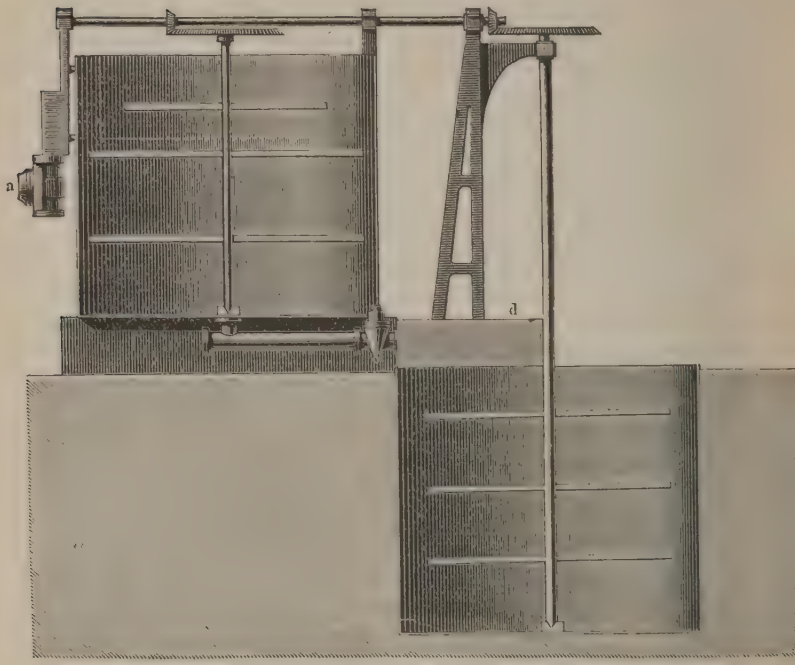


FIG. 236.

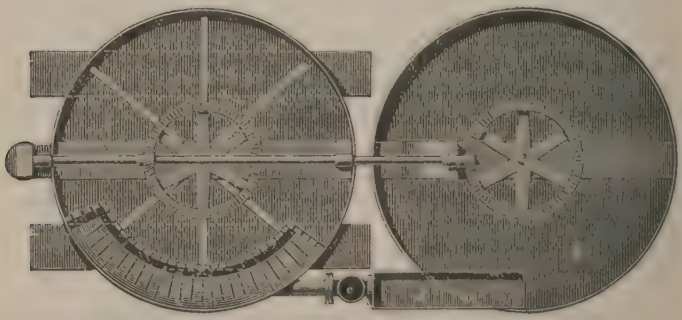


FIG. 237.

the automatic distribution of the milk-of-lime on several stills in a given order, consisting of several chambers with taps and overflows.

Peters (*J. Gasbeleucht.*, xlix., p. 163) describes arrangements for the automatic supply of lime-milk to ammonia-stills, and for preventing losses of ammonia from these.

Use of other Compounds for Liberating the Ammonia.

Magnesia is sometimes used in lieu of lime for decomposing salts of ammonia; but, apart from analytical purposes, only in such cases when it is intended to recover not merely the ammonia, but also the chlorine of ammonium chloride — a problem incessantly attacked, but not yet sufficiently solved, in the manufacture of soda by the ammonia process. It is, of course, an indispensable condition that the magnesia must be recovered, as its price prohibits wasting it like lime. The details of the many attempts made in this direction do not belong to the chapter on Ammonia Manufacture, but to that on Alkali Manufacture. We will therefore only briefly mention a very important patent of Messrs Pechiney & Co. (B. P. 9927, 1885). They found that the decomposition of solutions of ammonium chloride by magnesia, even at the boiling temperature, is only complete when the liquor is kept in a certain state of concentration, and they have accordingly constructed a still in which no steam is condensed, and no separation of NH_3 and water takes place, till the decomposition has been entirely accomplished. Only then the usual dephlegmation comes into play. *Cf.* p. 929 as to the greater difficulty caused by magnesia in comparison with lime.

D'Andria (B. P. 5762, 1888) and Chatfield (B. P. 6152, 1888) again patent the use of magnesia.

According to the *Alkali Report* for 1891 (No. 28, p. 88), one factory employs *caustic soda* for expelling the fixed ammonia. This is a clean process, but probably too expensive in most cases.

Cerium oxide, or the oxides or oxychlorides of other rare earths are employed by Whitehouse (Ger. P. 202350, of 1907) for obtaining free ammonia, together with chlorine or hydrochloric acid, from ammonium chloride. When heating NH_4Cl and CeO_2 to 100° to 350° C., NH_3 is driven off; the temperature

is then raised to 450° to 500°, and steam is injected, whereupon HCl is formed, or else by means of air free chlorine is obtained, $CeOCl_2$ remaining in the latter case. One mol. of $CeOCl_2$, heated with 2 mols. NH_4Cl, yields $CeCl_4$, whereby the cycle of the reactions is established.

Mode of Heating the Stills.

The apparatus for distilling gas-liquor differ in the mode of heating. This may be done either by a direct fire, or by open (wet) steam, or by indirect (dry) steam. Sometimes superheated steam is also employed. Expelling the ammonia by boiling alone, without employing the sensible and latent heat of the vapours evolved, consumes very much time and fuel. Hence in all modern apparatus this heat of the vapours is utilized for a preliminary heating of fresh gas-liquor and for driving out the volatile ammonia, and at the same time the gas is freed from aqueous vapour by dephlegmation. The additional first cost of a properly constructed apparatus is soon repaid by an enormous saving in fuel. Many kinds of apparatus have been devised for this purpose, a number of which will be described in detail later on; their principle is similar to that employed in rectifying spirit-of-wine or light tar oils (pp. 722 *et seq.*).

Which method of heating is most advantageous for distilling ammonia seems to be decided by the following experiments on a manufacturing scale made by Dr C. M. Tidy. A quantity of gas-liquor, amounting to 7000 gallons, requires—

	Hours.	Yields, as compared with the theory.
When heated by open fire from without	22	90 per cent.
„ „ indirect steam in a coil	18	92 „
„ „ open (wet) steam	14	98·5 „

This proves that steam directly blown into the liquor is by far the best agent, no doubt because its heat is thus most directly utilized, and perhaps even more so as the steam mechanically carries away the ammonia.

Safety-valves.

All stills intended for expelling ammonia without lime should be provided with safety-valves—a precaution not unfrequently neglected. The gas-delivery pipes easily get plugged up by ammonium carbonate, and this may lead to dangerous

explosions. Seidel (in Hofmann's *Report on the Vienna Exhibition*, vol. i., p. 96) and Watson Smith (private communication) testify to this. This danger is avoided by fitting up the boilers with safety-valves. These are, indeed, nowadays, compulsory in German ammonia-works.

Various products made from Raw Gas-liquor.

These products are :—Concentrated Gas-liquor, Pure Liquor Ammoniæ, Anhydrous Liquid Ammonia, Sulphate of Ammonia, other Ammonium Salts. We now proceed to describe their manufacture.

I. Manufacture of Concentrated Gas-liquor.

This product, consumed in large quantities in the manufacture of ammonia-soda, is made by a simple distillation of gas-liquor. It is a yellow liquid, smelling strongly of ammonia and sulphide of ammonium, containing 15 or 20 per cent. total NH_3. It serves also for manufacturing other ammonia salts which cannot be equally well prepared from raw gas-liquor, especially on account of the cyanide and sulphocyanide. At small gas-works this product is preferably made, as requiring less apparatus and no chemicals.

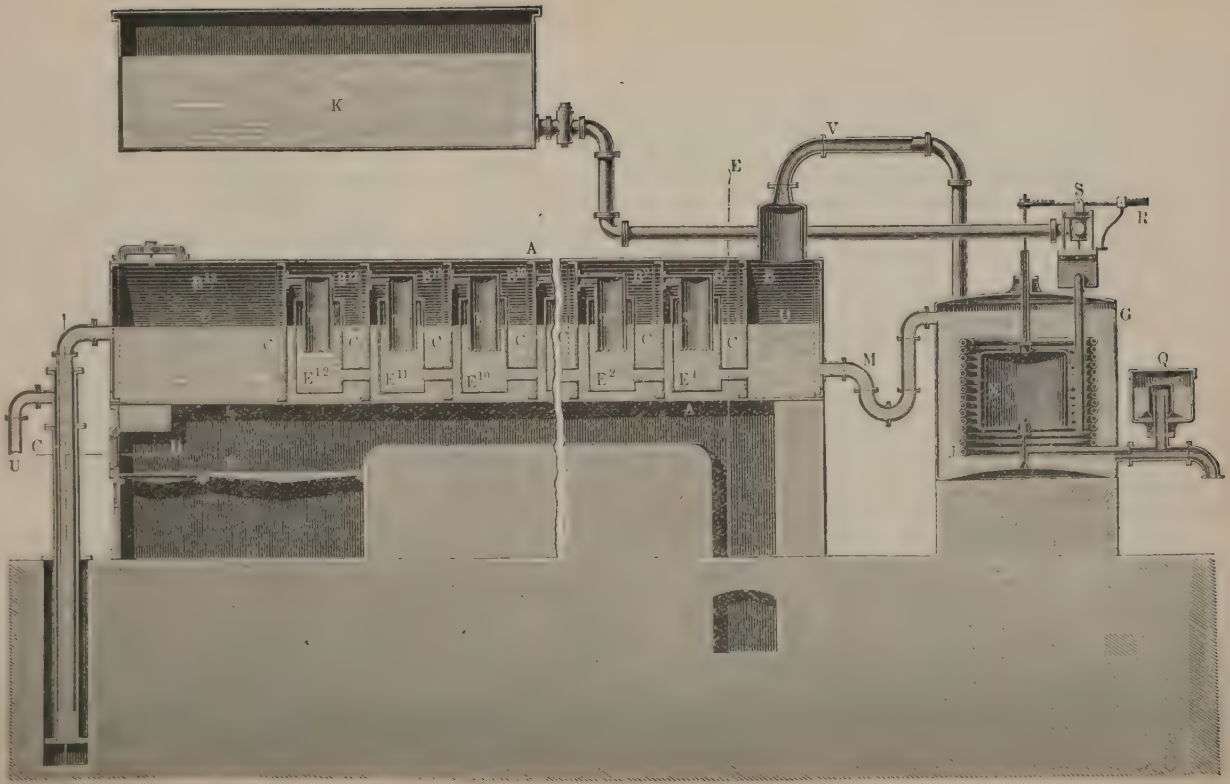
Sometimes two qualities of this liquor are made, viz., either less highly concentrated gas-liquor, containing from 16 to 18 per cent. total NH_3 and comparatively much CO_2, or highly concentrated liquor, containing from 18 to 25 per cent. NH_3 and but little CO_2.

Usually no lime is employed in this operation, but then no product should be aimed at of a higher concentration than the above, to avoid obstruction of the pipes by ammonium carbonate. Of course the fixed ammonia can be subsequently driven out by lime. If stronger liquor than the above is required, lime must be added from the first; the product will then contain mostly free ammonia and ammonium sulphide.

We shall now describe some of the best apparatus for this purpose.

Solvay's Apparatus (Fig. 238)

is specially intended to obtain concentrated crude liquor for ammonia-soda works, up to a strength of 15° per cent. NH_3.


K
V
E
S
R
A
G
Q
M
U
C
E^{12}
E^{11}
E^{10}
E^{2}
E^{1}

It consists of a still, A, divided by partitions C into a number of compartments. Each compartment contains a tank, E, connected with the next compartment at the bottom by a pipe. In the upper part of each compartment is fitted a pipe, T, which is enlarged below and carries the vapours into the liquid of the next tank. The fireplace is at D. The ammoniacal liquor comes from the store-tank K, and goes first into a small vessel, G, in order that the feed may be regulated by means of the valve attached to the lever R and the float X, and enters the still from the pipe M. Suppose this to be filled equally up to the level O. When vapours are evolved by heating the liquor, *e.g.*, in B^2, they escape by T and force a certain quantity of the liquid into the annular space between T and E^1, and over the margin of E^1 into B^1. Thus a certain quantity of gas-liquor is carried from B^1 to B^2 by means of the vapour evolved in the compartment B^2; in the same way the liquid travels from B^2 to B^3 by means of the vapours evolved there; eventually it arrives in B^{13}, and leaves that compartment by the pipe U. The progress of the liquid principally depends upon the proportion between the diameter of the dipping-pipes T and the vessels E. The vapours arriving in the last chamber B are carried by the pipe V into a worm, J, cooled by ammoniacal liquor, and afterwards through a washing-tank, Q, into the absorbing-apparatus. The float X regulates the flow of liquor into the still; it sinks as the liquid within the condenser is heated by the evolved vapours, and allows a larger quantity of liquor to enter through the valve S if the distillation goes on more quickly. When the firing is interrupted, no vapours are given off, the liquor ceases to pass from one compartment into another, and the level of the liquid rises; at the same time the float rises, and the valve S ultimately shuts off the feed of liquor entirely. According to Hanrez, the dimensions of the apparatus hitherto constructed are sufficient for concentrating, every 24 hours, 12, 24, or 48 cbm. (say tons) of gas-liquor of two or three degrees Baumé to the above strength, with a consumption of 27 to 36 kg. of fuel per cubic metre. The hot water running away from U can be utilized for a preliminary heating of cold gas-liquor.

Grüneberg's Apparatus for Direct Firing.

H. Grüneberg's older apparatus (Ger. P. No. 35, of 1877) has been superseded by a different form (Ger. Ps. 5255 and 9392), which alone we shall describe here. One of its principal

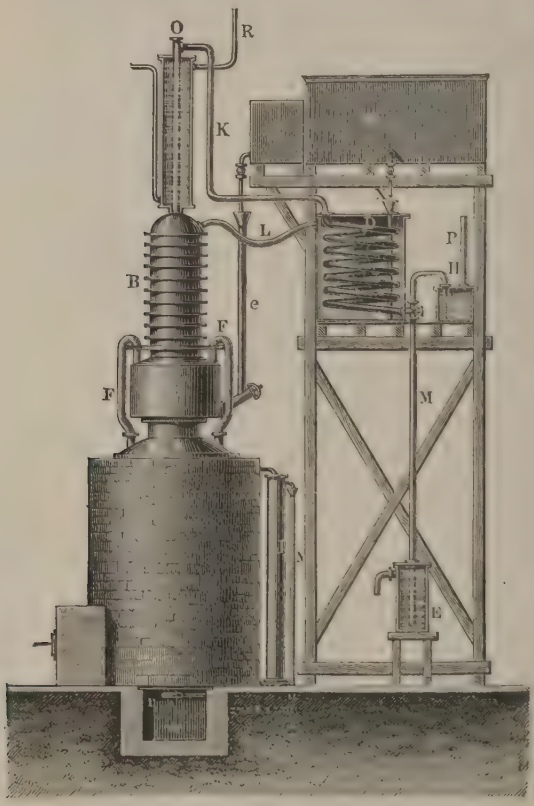


Fig. 239.

advantages is that it prevents the lime from forming hard crusts on the heating-surface of the stills, and removes the lime residue without any loss of time. Figs. 239 and 240 are partly elevations, partly sections. An upright cylindrical still, A, heated from the fireplace *w* by flues surrounding it, has

within it a vertical cylindrical tube, the bottom of which, extending below the bottom of the boiler, beyond its heating-zone, is closed and furnished with a blow-off cock, *r*, and a perforated screen. The upper end of this tube, reaching nearly to the top of the boiler, is open to the vapour-space in the boiler. Above the boiler is the vessel C, charged with milk-

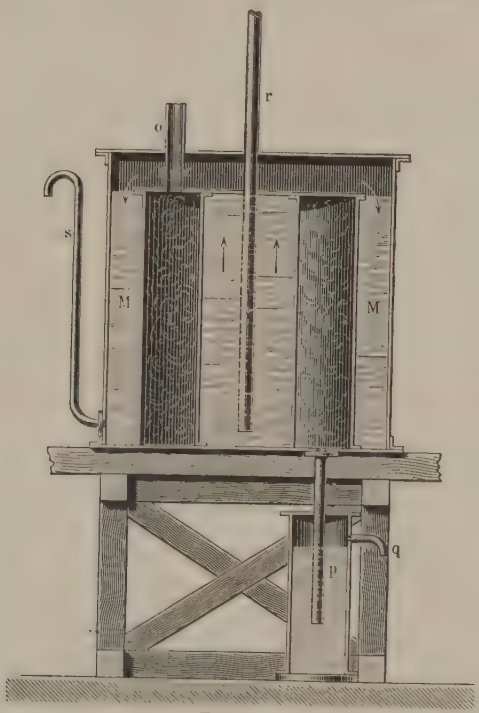


FIG. 240.

of-lime from the tank G by *e*, and above this a rectifying-column, B, of the kind often employed in spirit-stills. The pipes F F extend from the top of A into the lime-vessel, having near its bottom numerous small perforations. By these pipes the vapours generated in the still are conveyed into the milk-of-lime, and keep this continuously agitated; they then pass through the successive compartments of the column B. This column is supplied by the pipe L with gas-liquor, which

descends from one compartment to another, while the vapours ascending from A through C are intimately mixed with it. Thus the descending gas-liquor is gradually heated and deprived of its volatile ingredients, whilst the ascending vapours are partly condensed and mix with the descending liquid; the uncondensed gases, along with those liberated from the liquid in B, pass away through the pipe K. From the bottom of B the liquid, still containing the non-volatile ammonium salts, flows through an opening into the lime-vessel C and is mixed with its contents, the vapours from F F producing a continuous agitation. Here the ammonium salts are decomposed, and part of the ammonia passes along through B into K. The liquid, still containing ammonia, passes, by the overflow-pipes F, to the bottom of the boiler-tube, which is removed from the direct action of the fire, so that there is no danger of the lime becoming attached to the surface of the tube, neither can the material of the tube, or that of the lime-vessel, be injured by overheating.

From the bottom of the tube the liquid rises through the perforated plate, flows over into the outer boiler A, and is there heated; the gases and vapours evolved are conveyed by F F into C, as above mentioned. From the bottom of A the liquid, now entirely deprived of ammonia, overflows into a deep vessel, J, the contents of which operate as a hydraulic seal, and from this through N to a drain. All this proceeds *continuously*—the feeding with gas-liquor by L, the overflowing of the spent liquor by N, and the escape of the ammoniacal vapours at K.

The apparatus Fig. 239 serves for producing a concentrated solution of ammonium carbonate and sulphide, *e.g.*, for the ammoniacal-soda process. The vapours rise through the cooling-pipe O into a worm in the vessel D, where they are condensed to the condition of (impure) liquor ammoniæ. This flows into a vessel, E, whilst the uncondensed vapours and gas pass into a vessel, H, whose contents form a hydraulic seal. The gas not condensed here escapes through P. The vessel D is closed; and the worm within is cooled by raw gas-liquor supplied from the reservoir V by the funnel-pipe X; after getting heated here, it passes through L into the column B. The cooling-pipe O acts as a regulator of the concentration. The more cold water is supplied to its casing by the pipe R,

the greater is the condensation of aqueous vapour in O, the condensed water flowing back into B, and the more concentrated is the residual fluid which passes to the worm in D. Thus the degree of concentration of the liquid ammonia can be regulated at will.

If it were intended to make commercial liquor ammoniæ, the vapours issuing from the column would have to be passed through a number of vessels filled with milk-of-lime in order to retain CO_2 and H_2S and finally into a cooled absorbing vessel.

The worm D in Fig. 239, which is sometimes stopped up by crystallizations of ammonium carbonate, was later on replaced by a cooler, acting both inside and outside, as shown in Fig. 240. L is an annular iron vessel, fixed in the outer cylinder M. The ammoniacal vapours enter at *o*, condense in L, and the condensing-liquor runs off at *p* into a hydraulic seal, whence it runs over at *q* into the vessels intended to carry it away. The cooling-water enters at the bottom of the vessel, runs over the annular cooler L, and is carried off from this by another tube.

Grüneberg's apparatus has been superseded at most larger factories, but probably exists still in smaller works.

Grüneberg and Blum's Steam-still.

This apparatus, (Ger. P. 33320, of the Berlin-Anhaltische Maschinenbau-Ak.-Ges.) contains a cylindrical iron vessel, forming a reflux-cooler, the upper part being kept full of water, the lower part containing gas-liquor. The ammonia vapours, partly cooled here, are completely condensed by means of an iron worm as concentrated gas-liquor, and collected in a receiver. For each 100 kg. concentrated gas-liquor of 17 per cent. NH_3, 2·3 tons cooling-water of 13° C. is required. This still has also been superseded by more modern construction. So has also Ger. P. 64367, both of them shown in our former editions.

The Apparatus of the Berlin-Anhaltische Maschinenbau-Aktien-Gesellschaft.[1]

This firm supplies apparatus of their own construction

[1] This long title is practically abridged, by combining the initials, to the trade-mark "Bamag," used for all the apparatus of this factory, which are protected by numerous patents.

for all the branches of the manufacture of ammoniacal compounds.

Fig. 241 shows their *still for crude ammoniacal liquor.*

It consists of a number of cells, combined to a column, each cell being provided with steam pipes, covered by dishes nicked at the bottom, and with an overflow for the liquor; also with a

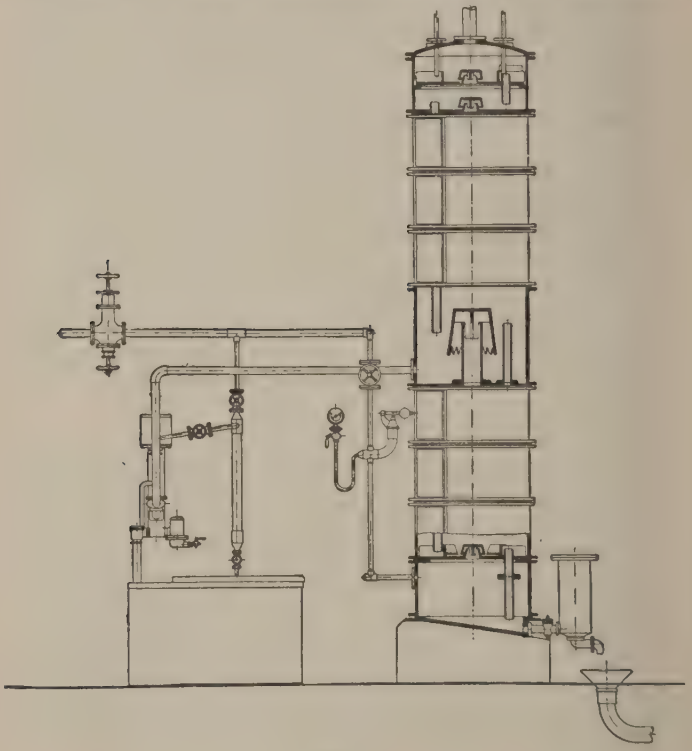


FIG. 241.

cleaning-hole. They are accessible in all their parts, so that the apparatus can be cleaned out without dismantling it. The pre-heated ammoniacal liquor enters into the top cell, the fresh steam at the bottom, so that it is compelled by the dishes to bubble through the liquor. The crude liquor is gradually heated to boiling, and yields its volatile ammonia, together with other

gases, to the steam in the upper half of the column. In a special, larger cell, visible about midway down the column, a more vivid motion is produced by means of the dishes dipping lower down in the liquor; here the milk-of-lime, required for liberating the combined ammonia, is introduced in slight excess and mixed with the liquor. The ammonia, thus set free, is driven out by further boiling in the lower half of the column. The spent liquor, which contains but 0·005 per cent. NH_3, leaves the apparatus by an automatically regulated outlet-valve, and can be usefully employed for pre-heating fresh liquor, as its temperature is about 100° C. The outlet-valve consists of a movable float of lead-coated sheet-iron, carrying the valve-cone on an iron rod. The float is placed in a cast-iron box and is under the same steam-pressure as the lower part of the column, so that the depth of water at which the valve opens always remains the same. The steam-inlet pipe bears a pressure-gauge, a steam-inlet valve and a safety-valve. The steam-pressure during the work is only from 0·1 to 0·3 atmospheres, the safety-valve blows off at 0·4 to 0·5 atmospheres.

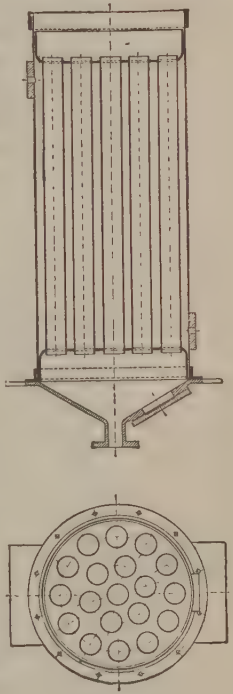


FIG. 242.

The pre-heating of the crude liquor takes place in tubular apparatus, Fig. 242, in which the hot-spent liquor descends in the tubes, while the crude liquor rises around them, and leaves the apparatus at a temperature of 70° to 80° C.

Fig. 243 shows the regulator for supplying the crude-liquor to the column. The supply is kept uniform by a regulator, and is measured by a tumbling-box, the movements of which are transferred to an index, showing the consumption of liquor in litres on a disk. For larger-sized apparatus the liquor is measured in a cast-iron piston-meter.

Very small columns may be fed by a hand-pump, but columns of any larger size require a steam-pump. The milk-

of-lime may also be introduced in several places, if desired. The pumps require no attendance except oiling and regulating at the outset.

An apparatus of the "Bamag" for producing *concentrated ammoniacal liquor* is shown in Fig. 245. Here A denotes a column-still, like that shown in Fig. 241. But since the mixture of steam, ammonia, carbon dioxide, and hydrogen sulphide,

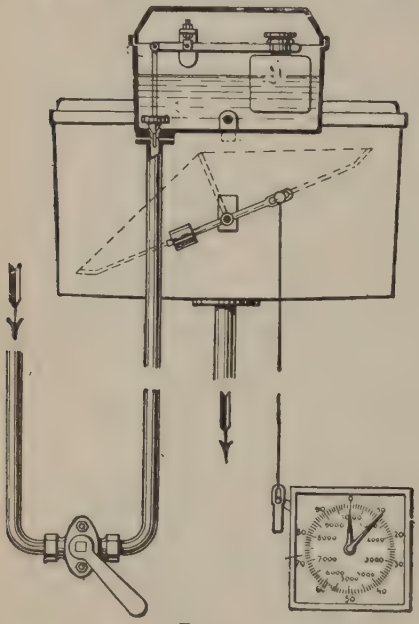


FIG. 243.

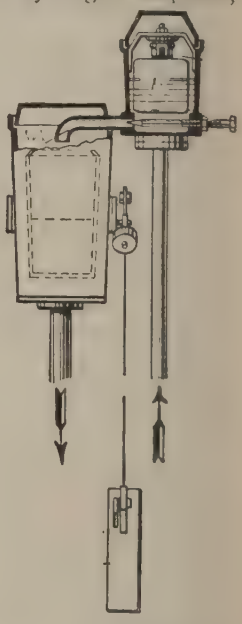


FIG. 244.

which issues at the top, must be deprived of steam to a sufficient extent before being allowed to condense again, it is made to pass through the *reflux-cooler*, B, which is shown on a larger scale in Fig. 246, in which the vapours are partially condensed and enough water is removed from them to furnish a sufficiently strong liquor when being completely cooled in the cell-cooler C. As the water condensed in B contains some NH_3, it goes back into column A.

In case of liquors, testing above 15 to 18 per cent. NH_3, the *carbonic acid* causes trouble, as the ammonium carbonate is then

separated in the shape of solid cakes which frequently stop up the coolers and tanks, and compel stoppages and cleaning operations, leading to much loss of ammonia. To prevent this,

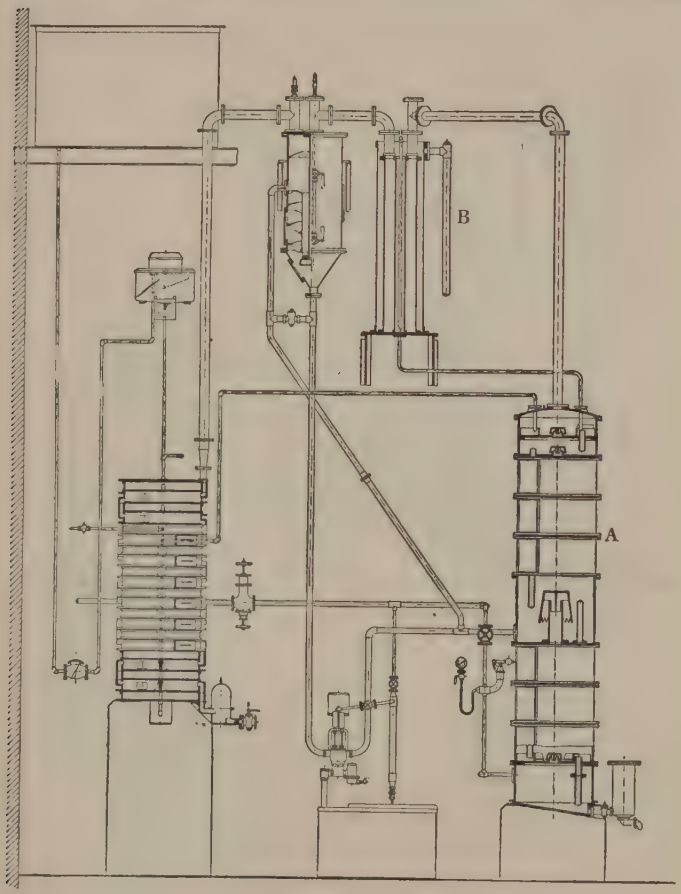


FIG. 245.

a special apparatus is interposed for the purpose of removing the carbonic acid. Up to 15 or 18 per cent. NH_3, this apparatus is not necessary, but such plant is only sufficient for small works. For properly concentrated liquor, testing from 22 to 26 per cent.

NH_3, *the* CO_2 *must be removed from the vapours by means of lime.* The apparatus for this purpose, shown at D in Fig. 245, is shown on a larger scale in Fig. 247. This *lime-washer* contains lead-

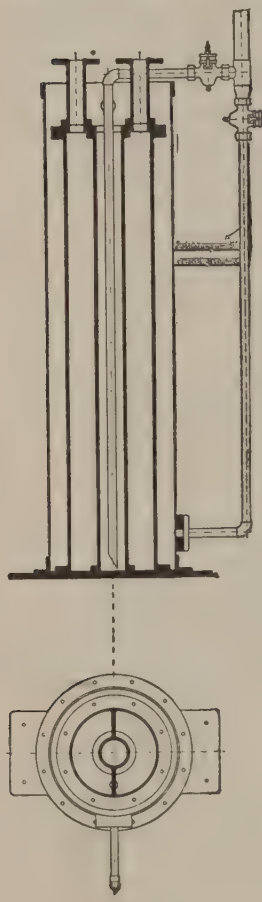


Fig. 246.

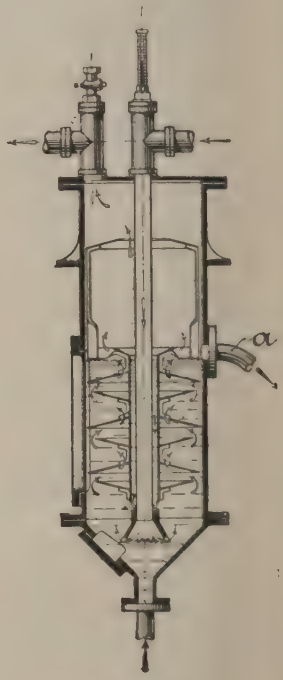


Fig. 247.

coated plates, placed round a central tube. Milk-of-lime is pumped in by pump E (Fig. 245) and runs over the plates, being constantly stirred up and carried upwards again by the gases and vapours passing through the apparatus. The strong

agitation of the liquid prevents the deposition of large amounts of calcium carbonate. The used-up milk-of-lime runs automatically back into the still A, where the NH_3 which it has taken up is recovered.

The cell-cooler, shown in Fig. 245, is shown on a larger

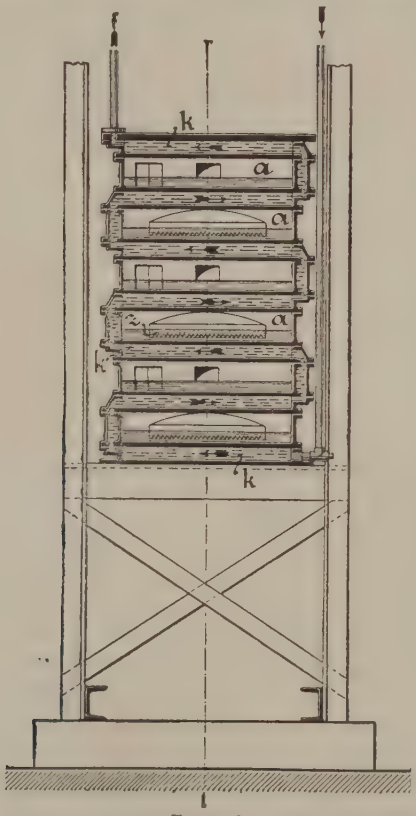


FIG. 248.

scale in Fig. 248. It consists of a number of ammonia-cells, *a*, provided with dipping sides, and cooling-cells, *k*, interposed between the ammonia-cells. Each cooling-cell at its top cools the water condensed in the next higher ammonia-cell, and at its bottom, the vapours in the next lower ammonia-cell.

The gases and the condensed liquor descend in the apparatus; the cooling-water taking the opposite direction. At the bottom the concentrated liquor flows into a tank-wagon or other portable vessel.

The "Bamag" also builds plant for manufacturing concentrated gas-liquor even in small gas-works; also apparatus in which the CO_2 is driven out by *heat*, founded on the principle that on heating the gas-liquor to 90° or 92° C., about one-half of the CO_2 and one-quarter of the H_2S are given off with very little NH_3. This heating is effected by the waste heat with which the liquor and the ammonia vapours leave the still, thus causing a great saving of steam, lime and labour. The details of this process are not given in their publications.

According to their Ger. P. 208254, of 1909, they place the ammonia still in flues, constructed in the chimney serving for the gas-generating apparatus, especially in cases where there is only one chimney for all of them. This allows small gas-works to work up their liquor without costly apparatus.

Various apparatus.

Thiel (*J. Gasbeleucht.*, 1907, p. 979) considers it preferable for small gas-works to make concentrated ammoniacal liquor by distilling with a direct fire, without lime and without the production of waste liquids. For this purpose he uses an apparatus constructed by C. Francke, in Bremen. This consists of a still with cooling-worm and receiver. Above the still is placed an open evaporating pan, heated by the same fire as the still. The gas-liquor is first distilled, until all NH_3 has been driven out and condensed in the receiver, to a liquid containing 10 per cent. NH_3. Then the residue remaining in the still is forced by its own steam-pressure into the upper pan, where it is concentrated by the waste-fire gases from a fresh operation in the still. This concentrated liquor, which contains only "fixed" ammonia, after cooling serves for washing the gases and is thus gradually enriched until it pays for sending out. The fuel required for treating a ton of gas-liquor amounts to 60 kg. refuse coke.

Fillunger (Austr. P. 27071) distils the gas-liquor without lime; the residual liquor, after cooling, is passed again through the gas-washers and the stills, and this is continued for a long

time, so that the formation of large quantities of waste liquor is avoided.

Kremer (Ger. P. 151980) injects hot air into the ammonia-still, in order to break up the drops of liquor and to enlarge the surface to be heated.

Carr (B. P. 16978, of 1898) employs a number of pipes, one above the other, and superheats the vapours, in order to promote the conversion of the cyanides into ammonia.

Carpenter (B. P. 22518, of 1906) patents some modifications of the usual ammonia steam-stills.

The Apparatus employed in Ammonia-Soda Works

is not described here, but reference is made to the author's *Sulphuric Acid and Alkali*, vol. iii., where full details are given respecting its use in alkali-works.

Concluding remarks.

The prevention of nuisance during these operations will be described in connection with the apparatus for the manufacture of sulphate.

The *testing* of concentrated gas-liquor is effected in the same way as that of crude liquor, *supra*, p. 926 *et seq.* Sometimes it is performed by simply boiling the liquor, diluted with 10 times its bulk of water, with an excess of standard acid and retitrating with standard soda.

II. Manufacture of Pure Liquor Ammoniæ.

This is the most difficult, but the most remunerative way of dealing with gas-liquor, and is practised on a very large scale, the demand for this article for cold-producing machines being very great.

Liquor ammoniæ is a more or less pure and concentrated solution of caustic ammonia in water. Beside ammonia it frequently contains compound organic bases and other tarry products, which impart to it a disagreeable smell, and sometimes also a yellow or brownish colour. This yellow (amber) colour is often not present in the freshly prepared liquor, but is developed from the empyreumatic substances in course of time, especially under the influence of sunlight. The liquor

ammoniæ derived from sewage, directly or indirectly, contains hardly any of these impurities, while that derived from gas-liquor is sometimes very much contaminated with them.

Formerly liquor ammoniæ was prepared by distilling sal-ammoniac with slaked lime; and for analytical purposes this is still sometimes done, but even then only exceptionally, since the ammonium sulphate is very much cheaper than the chloride. When employing sulphate, it is usual to carry on the operation in a cast-iron still provided with an agitator, to prevent a crust of calcium sulphate from impeding the further reaction of the lime upon the ammonium salt. Even from sulphate very little caustic ammonia is now made, since it is easy to make it directly from gas-liquor, in one or two distillations.

When making liquor ammoniæ directly from gas-liquor or any other ammoniacal liquor containing principally ammonium carbonate and sulphide, sufficient lime must be added from the outset to retain the carbon dioxide and hydrogen sulphide. This may entail much trouble in consequence of crusts of lime forming on the walls of the stills, which must be overcome by special means. When white and pure caustic ammonia is required, the empyreumatic substances must be absorbed in a suitable manner or destroyed. The most usual way of doing this is filtering the vapours through recently ignited wood-charcoal. Some recommend, as more convenient, passing the vapours through a fatty oil, which retains the tarry substances, and can be again partially freed from them by heating; or else redistilling the liquor with potassium permanganate. But these means are rarely employed, as they are in reality more troublesome and expensive than the use of wood-charcoal, which can be repeatedly used after ignition each time in closed vessels, and when quite inactive for filtering the vapours it is still good for fuel.

Watson Smith[1] advises in any case, even when liquor ammoniæ is the principal product, to make along with it a little sulphate, because the gas which first and somewhat tempestuously escapes in the distillation carries along with it some tarry matters, and hence is best not employed for making liquor ammoniæ. This of course cannot be observed in the continuously acting apparatus to be described below; but

[1] Private communication.

even then mostly only crude strong ammoniacal liquor is at first obtained, from which liquor ammoniæ is prepared by distilling into pure water. In order to carry off separately the first evolved portion of ammoniacal gas, the gas-delivery pipe of the ammonia-still is provided with two branches, each of which is shut off by a stopcock, or by a short piece of 2-inch indiarubber pipe with a screw clamp, so as to direct the vapours either into the ordinary saturating vessel filled with sulphuric acid, or into a worm for condensing crude liquor ammoniæ. The latter is collected in large iron tanks, from which the vapours pass first through a barrel half-filled with water, or preferably, to avoid pressure, through a lead worm, serving as a reflux condenser, in which the vapours ascend and are met by water trickling down from a funnel, to condense the last traces of ammonia. (No doubt a small coke-scrubber fed with water, or preferably with sulphuric acid, would act even more thoroughly.)

From this crude liquor (or any other crude concentrated ammoniacal liquor) pure liquor ammoniæ is prepared by many descriptions of apparatus. A very simple form, which was in operation at a Manchester works some years ago, is shown in Fig. 249. The liquor is put into a circular still, *a*, 8 ft. long and 4 ft. in diameter, heated by a fire which is kept away from the bottom of the still by an arch, and only circulates round the sides. For each charge of 600 gallons, containing $3\frac{1}{2}$ to 4 per cent. ammonia, 2 cwt. of quicklime, previously slaked to a thick paste, is added and a strong fire is made. The gases escape through a 2-inch pipe into a lead worm, *b* (cooled outside by water), in which the aqueous vapour is condensed and flows back. In the descending branch *c* a little water is condensed and collects in the carboys *d*. The nearly dry gas is treated in the purifier *e* (6 ft. long and $4\frac{1}{2}$ ft. wide) with slaked lime, to remove hydrogen sulphide, tar, etc. The top of the purifier is luted with lime-putty and is screwed down tightly; its contents must be renewed two or three times a month. From this the gas passes in a 1-inch pipe through a small washing-arrangement, *f*, and then, by means of indiarubber joints provided with screw-clamps, at will into one of the three absorbers, *g*, *h*, *i*, made of iron lined with lead, $3\frac{1}{2}$ ft. square and 3 ft. high, and provided with gauge-glasses.

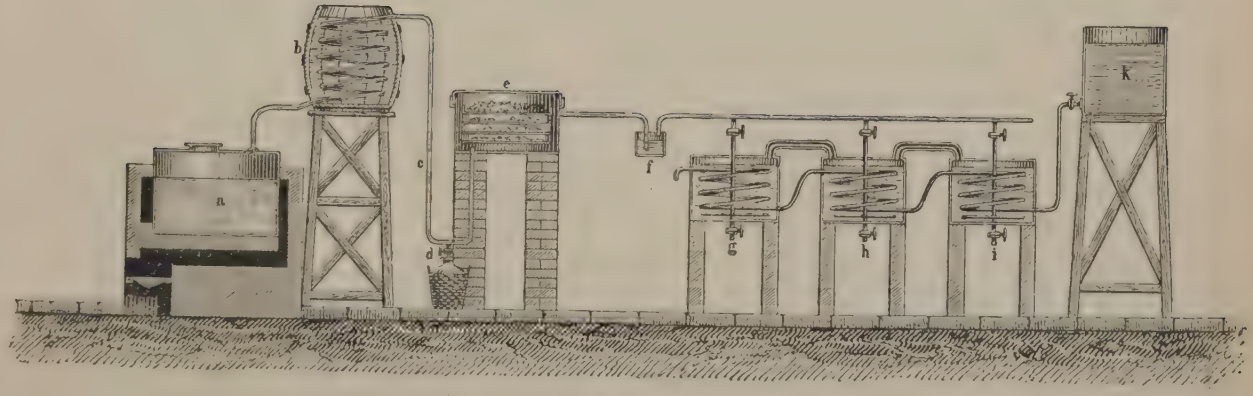


FIG. 249.

These vessels are charged with pure water; the gas issues into them from perforated rings of lead tubing lying at the bottom. These vessels are connected by gas-pipes; they also have an air-vent each, but of course this is only opened in the last one of the series. The contents of *g*, *h*, *i* are cooled by water, which, coming from the tank *k*, is passed through all the absorbers by means of worms. After the liquor has become sufficiently strong, it is drawn off by taps into carboys, ready for sale. It should be clear, free from any greasy matter, and of sp. gr. 0·905, or at most 0·914. No traces of sulphides, indicated by lead acetate or sodium nitrocyanide, should be present. (This description may serve to show how an apparatus can be constructed in a cheap and simple manner; but it lacks some of the qualities of more modern appliances.)

Apparatus of Elvers and Pack.—Fig. 250 is a sketch of this "two-boiler" apparatus for making liquor ammoniæ direct from gas-liquor. We have not reproduced the original sketch, which is somewhat difficult to understand, but placed the parts separately alongside each other, to make the principle clearer. For the same reason all supports, carrying-walls, etc., are left out. A and A′ are cylindrical iron boilers, A′ being placed sideways and above A, which alone is directly heated by the fire. A is surmounted by a dome, to which is attached an air-valve *v*, for avoiding a collapse of the still by the atmospheric pressure on cooling, and the gas-delivery pipe *a*. The latter is carried first up, then down, and enters A′ near the bottom, continuing into a pipe running all along the bottom and perforated with many holes, through which the vapours from A get into A′. The liquid in A′ can be run into A by means of the wide pipe and valve *m*, which can be cleaned from deposit by means of a suitable contrivance. The vapours arising in A′ first ascend in *b*, then descend into the vessel B to within 12 inches of its bottom; the liquid condensed in B runs through *l* into A′ below the level of the liquid there. From B the vapours pass into the worm C, and through *c* into the closed box D. From this the condensed liquid can be run back into A′ by the tap *s* and the pipe *p*. D carries a safety-tube, *d*, and a pipe, *e*, for taking away the uncondensed gases. These, now mostly freed from moisture, pass into the four cast-iron pipes E E′ E″ E‴, connected alternately at top and bottom by the

pipes *f f' f''*; they are open at both ends, and closed by plates

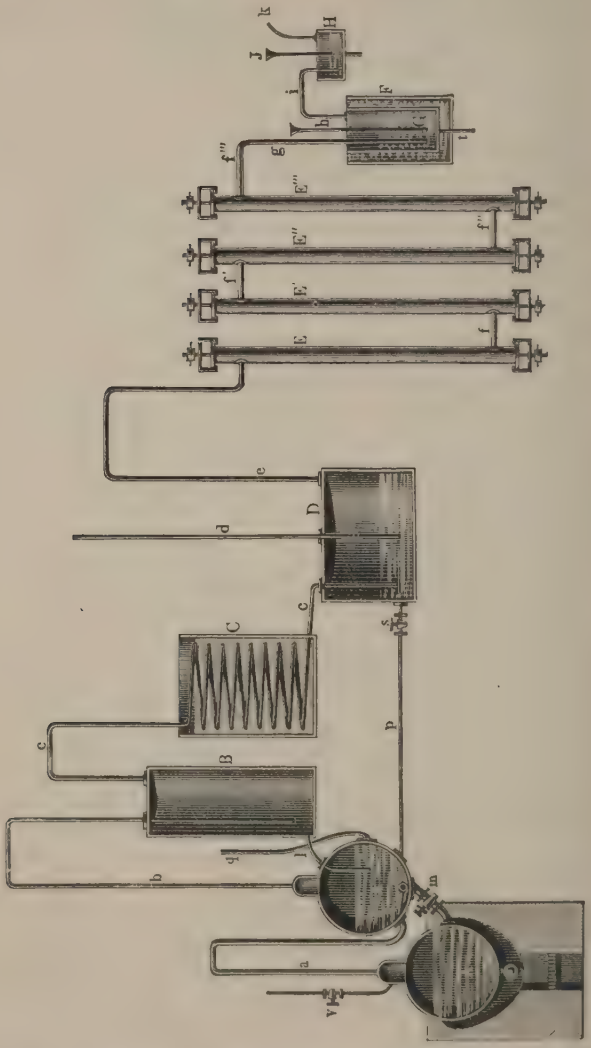


FIG. 250.

tightly screwed down. From E''' the gas travels through *f'''* and *g* into the leaden absorbing-vessel G, placed in a cold-water

tank F; here also a safety-pipe, *h*, and a discharge-pipe, *t*, are provided. The residual gas escapes through *i* into a small absorbing-vessel, H, with safety-pipe J; and *k* carries the incondensable gases into the outer air.

First the still A′ is charged by the pipe *q* with about 1000 litres of gas-liquor, contained in a higher store-tank; and this is at once mixed with a sufficient quantity of lime through a special aperture. The valve *m* is opened; the condensers C and F are charged with cold water, the pipes E E′ E″ E‴ with freshly ignited wood-charcoal in pieces the size of a walnut, and the covers are screwed down. G is charged with 60 or 65 litres of water, H with ½ litre. When the liquor mixed with lime has run from A′ through *m* into A, *m* is closed and the fire is lighted. The fire-gases travel along one side of the boiler, return along the other, and then go to the chimney. When the contents of A begin to boil, first the air is expelled and passes in bubbles through the water in G and H; A′ and the pipes are filled with vapours and become heated. Gas-liquor is now run through *q* into A′; by the cooling thus produced, the liquor in D is sucked back into A′ through *c* and *b*, and air enters at *d*. When 1000 litres of gas-liquor have run into A′, milk-of-lime is again added and well mixed, whereupon the fire is started again. The ammoniacal vapours from A escape through *a* into the liquid in A′, traverse this from the many small holes in the pipes, and give off part of their ammonia to it. A portion of the steam is condensed in B, the water running back into A′ through *l*, along with the volatilized salts. From B the vapours pass into C, where most of the water, together with a portion of the ammonia, is condensed. The condensing liquid serves for washing the ammoniacal vapours, and especially for retaining the salts carried away with them. The uncondensed vapours pass through *e* into the charcoal-purifiers, which absorb the impurities mixed with the ammonia-gas. In G the pure ammonia-gas is condensed by cold water, and liquor ammoniæ is obtained. The last remnant of the ammonia is absorbed in H by sulphuric acid; the incondensable gases escape through *k*. When the still A is worked off, the residue is discharged, and it is recharged from A′. The liquor now reaspirated from D into A clears the worm C, etc., from any deposit. If in G and H ordinary water, not distilled, has been employed for

absorbing the ammonia, the precipitate of calcium, aluminium, and magnesium salts formed must be allowed to settle in order to obtain a clear, marketable product. Each operation takes 4 or 5 hours; and from 1000 l. of gas-liquor of 3° Baumé is obtained 100 to 110 kg. of liquor ammoniæ of 32° Baumé (=sp. gr. 0·924).

The Berlin-Anhaltische Maschinenbau-Aktien-Gesellschaft ("Bamag") supply the apparatus, shown in Figs. 251 to 254, for the manufacture of pure liquor ammoniæ. The vapours coming from the *column-still a*, provided with automatic outlet-valve *b* (*cf.* p. 982, Fig. 241), are partially cooled in the reflux-cooler *c*, so that only small quantities of water pass over with the ammonia. The remaining gases are completely freed from CO_2 and H_2S by the three carbonic-acid washers *d d d*, constructed as shown in Fig. 247, p. 986, for concentrated gas-liquor, the milk-of-lime flowing into the last of these at the top, and descending into the second, lastly into that at the bottom. *e* is a "lime-catcher." From here the milk-of-lime is pumped into the column *a*, where the free lime still present decomposes the non-volatile ammonium salts. In *d d d* the CO_2 and H_2S are retained by the lime, and the gases pass though two coolers, *f f*, with the receiver *g*, and a coke-filter, *h*, where the ammonia-gas is further dried and purified. An oil-washer, *i* (*cf.* p. 990), removes most of the fetid organic substances, and any remaining impurities are retained by the charcoal-washers, h_2 and h_3, from which the ammonia-gas issues in a perfectly pure state. It is retained in the circular, properly cooled absorbers *k*, the last of it in *l*, and furnishes liquor ammonia of any desired strength; *m* is a steam-pump for fresh milk-of-lime, *n* is a pump for pumping the milk-of-lime from the carbonic-acid washers into the still *a*, *o* an apparatus for distilling water, *p* a tank for receiving this, *r* a centrifugal pump for supplying it to the still *a*.

Recently the "Bamag" employs for the manufacture of liquor ammonia the process of *driving out carbon dioxide by heat* (*cf. supra*, p. 988, and *infra*, p. 1003), in which the preheated crude liquor is heated up to 92° C., and the remaining CO_2 is saturated by lime in an agitating vessel, whereupon it passes into the still, and from there the NH_3, which is now in the free state, mixed with steam, and, after previous partial cooling, goes

on to the reflux-cooler. The further purification by charcoal, oil, and soda-filter goes on as usual.

Heinrich Hirzel's apparatus (Figs. 255 and 256) produces

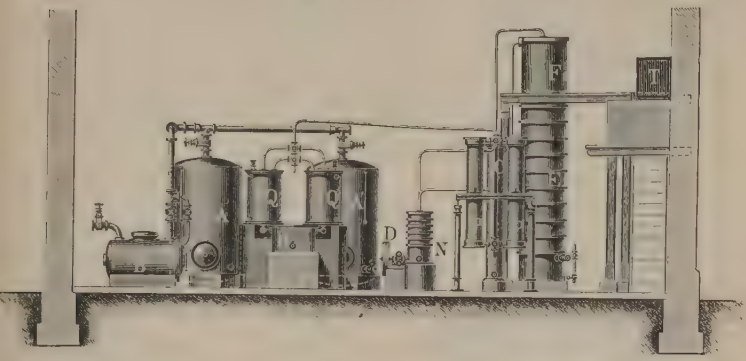


FIG. 255.

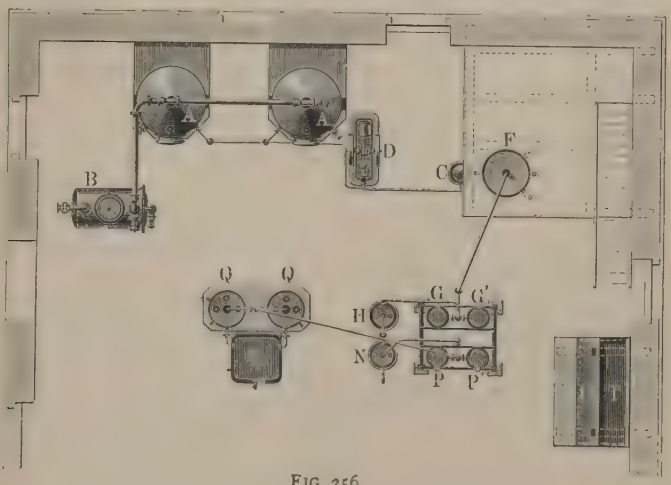


FIG. 256.

chemically pure liquor ammoniæ of maximum strength (28° to 30° Baumé.). A and A′ are decomposing-vessels, alternately charged with gas-liquor and lime, the mixture being previously made in B. The contents of A and A′ are gradually pumped

by P into the heater F, forming the upper part of column E, into the bottom of which steam is blown. The condenser F dehydrates the gas, which yields its impurities in the washers G, H, N, and P to milk-of-lime, oil, and charcoal; the pure gas passes through P into the cooled absorbers Q and Q', and from these into receiver R. T serves for preparing distilled water, collected in U, and serving to feed Q and Q'; 97 per cent. of the ammonia can be thus recovered; the waste liquor from the column contains but 0·01 per cent. NH_3.

Feldmann (B. P. 11711, of 1884) operates in quite a different way. He objects to the employment of lime-washers, etc., after distillation; his principle is, employing a sufficiency of lime *before* distillation, and separating the precipitate formed after some time by means of a filter-press. In lieu of the greenish, slimy residues otherwise produced, which are very difficult to dispose of, there are obtained, by means of a filter-press, solid cakes, from which the last portions of ammonia are recovered by a washing arrangement and by excluding the air during the operation. The filtered liquor is now distilled in a column, and the distillate can be brought up to 25 per cent. NH_3, but is still an impure liquor, since the ammonium sulphide is not decomposed by the cold treatment with lime. It is, however, completely decomposed by redistilling with an excess of lime, say, twice the theoretical quantity. As the quantity of liquor is now very small, and the ammonium sulphide on the average is only one-twentieth of the total ammonia, there is no difficulty whatever in that redistillation, especially as the calcium sulphhydrate is produced in a liquid form.

P. Mallet recommends his column provided with a mechanical agitator (*cf.* p. 1047) as being particularly adapted for the manufacture of caustic ammonia, where a large excess of lime must be employed.

In order to make white liquor, he employs the apparatus shown in Fig. 257. Here A is a cast-iron column, 1 foot 6 inches wide, formed of 14 chambers containing a solution of caustic soda, introduced by the funnel *a*. B is a similar column, containing a vegetable fatty oil, or heavy mineral oil, for retaining the empyreumatic substances (p. 990); G, a wrought-iron tubular saturator, through the tubes of which a current of cold water is constantly passing, to cool the liquor during the

condensation of the ammonia; D, a cast-iron safety vessel, in which the gas escaping the action of water in the saturator D is retained. The gas coming from the ammonia-still (where plenty of lime has been employed) enters at E into the column A and there parts with most of its impurities, and is completely causticized; in the column B most of the organic alkaloids and empyreumatic substances are retained by the oil; the purified gas meets with cold water in the saturator G; and when the solution is strong enough, it is run off by the tap *p*. The liquor

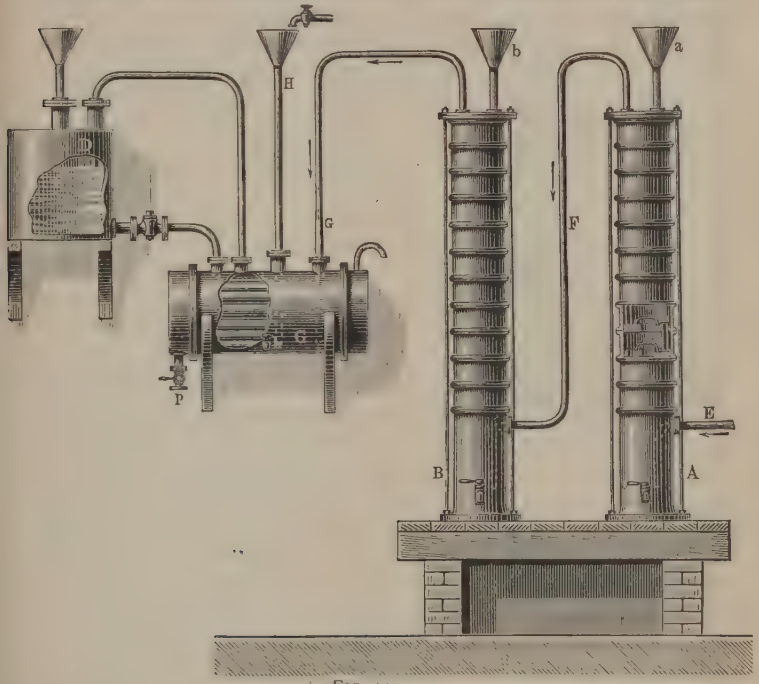


FIG. 257.

contained in D is now run into G; B is refilled with pure water, and the operation is started again. The liquor ammoniæ thus made keeps white even in the sunlight; but it still contains traces of foreign products, as is proved by its being more or less coloured brown by nitric acids. Liquor which is to stand this test as well must be made from sewage liquors.

Improvements to this apparatus are contained in the patents of Mallet & Pagniez (Ger. Ps. 31003 and 66288).

Rousseau (Fr. P., August 18, 1880) recommends that, in rectifying ammonia by dephlegmation, the water should be kept at a temperature of from 60° to 70° C.; below this, *e.g.*, at 55°, the liquor begins to take up ammonia from the gases passing through.

Hegener (Ger. P. 11669) prevents the escape of ammonia in charging with milk-of-lime by means of two tanks placed above the still. In the upper one (R, Fig. 258) the lime is slaked, and the milk-of-lime is let down into the lower one, R′, by the cock H. During this the ammoniacal gases in R are conveyed to a special receiver by a pipe proceeding from the air-cock B. When the milk-of-lime is to be run into the still, the cocks H and B are closed, but H′ and the steam-cock D are opened.

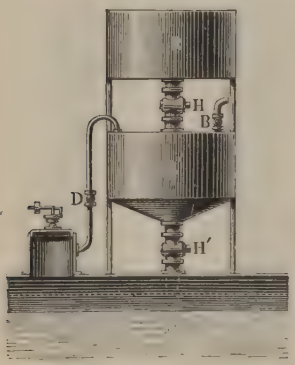


FIG. 258.

An apparatus patented by the Société anonyme des produits chimiques du Sud-Ouest (Ger. P. 13429) does not seem to offer any special advantages over those already described.—That of Rube, Engelcke, and Krause (Ger. P. 15570) consists of a column formed of a number of funnels superposed one over another, into which ammoniacal liquor and milk-of-lime are introduced by separate siphon-pipes.—G. Wunder (Ger. P. 17411) employs the old principle of two boilers, one for the volatile and one for the fixed ammonia, the latter being heated by the steam coming from the former, which itself is heated by a fire.—J. Gareis (Ger. P. 21707, B. P. 3164, of 1882) employs a combination of four vessels, so arranged that the one filled with milk-of-lime is not, like the lowest, heated by a direct fire, but by the steam coming from the latter, just as is done (in a more perfect way) in the Grüneberg stills, p. 984.—F. Gerold and M. Vacherot (Ger. P. 21821) patent a travelling apparatus for working gas-liquor, consisting of a simple cylindrical boiler, with an inside fire-tube, like a Cornish boiler, resting on a

railway truck. [This form of boiler is quite unsuited for distilling gas-water, especially with lime, as proposed by the inventors.]—C. H. Schneider's apparatus (Ger. P. 21252) is a two-boiler still with dephlegmator, without any essential difference in principle from the ordinary apparatus.—The same also applies to the apparatus of C. Berson (B. P. 11449, of 1884), which contains a directly fired retort of peculiar shape. C. Hills (B. P. 5874, of 1884) heats the gas-liquor as it descends in a scrubber, the heat being applied to the lower part of the scrubber. By this means the temperature of the descending stream of gas-liquor is gradually raised, and most of the sulphuretted hydrogen and carbonic anhydride, and some ammonia, are expelled, the latter being absorbed by the cool gas-liquor in the upper part of the scrubber, whilst the H_2S and CO_2 pass away from the scrubber.

Chur (Ger. P. 166973), in order to purify the NH_3 driven out from gas-liquor from H_2S and CO_2, passes the gas, by means of hydraulically luted bells, through milk-of-lime. In order to compel the gas to remain a long time in contact with the milk-of-lime, without unduly increasing the hydraulic pressure, there is an arrangement of vertical partitions, dividing the space below the bells into a number of chambers through which the gases have to pass in succession.

In a later patent (Ger. P. 188814) Chur places a special decomposing-vessel (lime-mixer) on the top of the distilling-column. In this vessel the preheated concentrated crude gas-liquor, is mixed with lime and heated by steam, *without dilution.* Thus the ammonia is completely split off from the CO_2 and H_2S, and even part of the non-volatile ammonium compounds are decomposed, the remainder being easily decomposed in the column below. Thus the principal quantity of ammonia is already obtained in the lime-mixer, and it is easy to treat there gas-liquor of high percentage, up to 15 to 20 per cent. NH_3. This takes place because most of the lime is already used-up in the mixer, and the mud, passing through the column, along with the gas-liquor, contains lime mostly already neutralized, so that even on working a concentrated liquor, the columns do not get obstructed. At the same time the consumption of lime and steam is less than usual.

Dr C. Otto & Co. (Ger. P. 174695) employ the liquor from

the reflux-cooler for washing the gases to recover any NH_3 escaping.

Maréchal (Fr. P. 350679) removes the sulphur of gas-liquor by means of ozone; the precipitated sulphur is sold in a compressed state.

Hartmann (Ger. P. 164723) describes a pump for both raising and stirring up the milk-of-lime. Two pumps are combined, one of them being connected both ways with the lime-tank and causing a constant circulation of the milk-of-lime; the other pump is connected on the one side with the lime-tank, on the other side with the still, and both are driven by the same mechanism.

Carl Menzel Söhne (Ger. P. 165098) describe a pump for mixing and automatically dividing the milk-of-lime among several stills. An automatic lime-pump is also described by Kordt (*J. Gasbeleucht.*, 1903, p. 375).

Keppich (Ger. P. 125573) separates ammonia from the organic amines present, by passing the mixture of bases, expelled from the still, through a series of absorbers, charged *seriatim* with the equivalent of acid corresponding to each of the bases present, the proportion of which must be previously ascertained by analysis. Thus, he asserts, the bases are separated according to their relative chemical affinity to the acid contained in the absorber.

Coppers (Ger. P. 140350) employs a closed saturator, and allows the steam formed therein to preheat the gas-liquor in a special column from which the main column is fed.

Doersch (U.S. P. 709846) describes an ammonia generator for laundry purposes.

Naef (Ger. P. 115249) evolves pure ammonia from ammonium chloride and magnesia in a continuously acting chamber.

The following patents can be mentioned only by name:—Henderson (B. P. 15836, of 1885); Brison (Ger. P. 34030); Pampe (described in Fehrmann's *Ammoniakwasser*, 1887, p. 67); Chevalet (B. P. 8819, of 1886); Holgate (B. P. 3384, of 1890); Whiteside (U.S. P. 534935); Bachmann and Sulzer (U.S. P. 573956); Stroh and Osins (U.S. P. 710221); Brunck (B. P. 8287, of 1903); Hirzel (Ger. Ps. 88953 and 91717); Francke (Ger. Ps. 165309 and 169444); Abendroth (U.S. Ps. 712891 and 792379); Adriaanse (Fr. P. 355971).

Cf. also the apparatus described *infra* for sulphate of ammonia.

Removal of Sulphuretted Hydrogen and Carbon Dioxide without Lime.

A number of processes for obtaining pure ammonia is based on the fact that on heating crude gas-liquor to about 90° or 95° C, the CO_2 and H_2S split off from the NH_3 and escape while the NH_3 remains behind in the liquor and can be driven out later on by raising the temperature. We shall describe the more important of these processes, having touched upon some of them *supra*, pp. 988, 996, 1001.

Pfeiffer (*J. Gasbeleucht.*, 1900, p. 89) points out that in the manufacture of liquor ammoniæ the previously heated gas-liquor usually contains two-thirds of the ammonia in the free state, which can be driven off without lime. During the heating up to 100°, mostly H_2S and CO_2 escape, with a little NH_3; these gases are passed through crude gas-liquor, in order to retain the NH_3. The quantity of lime necessary for driving off the fixed ammonia is previously ascertained by the method indicated below; but in order to be on the safe side, about 30 to 50 per cent. more lime is slaked to cream and is pumped into the gas-liquor, heated as above, after which the distillation is carried on with open steam. The ammonia-gas, containing aqueous vapour together with a little H_2S, CO_2, and empyreuma, has to pass three milk-of-lime washers, a reflux-cooler, and four charcoal-filters, and is then absorbed in distilled water. The distillation of 3 tons liquor requires 8 hours (the heating up to 100° another 2 hours). The residue in the still contains only 0·03 per cent. NH_3, which it does not pay to recover. The finished liquor ammoniæ never contains any sulphide, even when only the theoretical quantity of lime has been employed, and any such contamination can be wholly avoided by interposing (as has been done at the Magdeburg gas-works) between the last charcoal-filter and the absorber a *caustic soda washer*, charged with a 10-per-cent. solution of caustic soda. This consists of a cylinder of $\frac{3}{16}$-in. sheet-iron, 2 ft. 8 in. wide, 2 ft. 3 in. high, with an inside bell, 2 ft. 6 in. high, 1 ft. 10 in. wide, perforated in its lower portion (up to 12 in. high) with a number of $\frac{3}{8}$-in. holes. The gases pass up the centre, escape

through the holes under very slight pressure into the outer space, and away from this to the absorber. The sucking-back of liquid from the latter is prevented by an open water gauge-pipe attached to the washer, about 10 feet high. One filling of this apparatus lasts many months, as it is used only in cases of accident, which are thereby rendered harmless. It also dispenses with the necessity of renewing the lime in the "hot washers," which consequently act only as water-separators.

The whole of the apparatus on Pfeiffer's system employed at the Magdeburg gas-works is shown in *J. Gasbeleucht.*, 1903, pp. 1 *et seq.*, and in *J. Soc. Chem. Ind.*, 1903, p. 142.

Pfeiffer's method for ascertaining the quantity of lime required for distillation simply consists in boiling in an open flask 25 or 50 c.c. of raw (or 100 c.c. of previously heated) gas-liquor with 20 c.c. of a milk-of-lime containing 2·8 g. CaO, after diluting to 200 c.c., until all the ammonia is expelled (which takes $\frac{1}{2}$ or $\frac{3}{4}$ of an hour after the liquid has been got up to ebullition), cooling down the residue, diluting with water, and titrating back with normal hydrochloric acid and phenol-phthalein. Each cubic centimetre of the acid = 0·028 g. CaO; by deducting the CaO still found in the residue, the quantity consumed during the reaction is ascertained.

Solvay & Co. (Ger. P. 49500) remove CO_2 and H_2S by means of column S (Fig. 259), composed of chambers b to b_4, each of which contains a worm connected outside by the joints w to w_3. Each chamber communicates with the next above by necks d_1 to d_4, covered by hoods e_1 to e_4, and with the next below by overflows f_4 to f_1. The vapours from still A pass through column S into the condenser C, the liquid from this running through s into X. C also consists of a number of chambers, g, connected by overflows, a worm i passing right through. From the bends w to w_3 reflux-pipes z carry the condensed liquid to a collecting-pipe, u, and from this through v back into the still. The worm i is at the bottom connected by pipe n with the gas-liquor tank H. The liquor, heated up in the worm i to about 40° C., passes through o into washer W, where it takes all the NH_3 out of the vapours escaping from b_4, through m, but allows all the CO_2 and H_2S to escape through m_1.

Through the descending pipe p the liquor runs from washer W into chamber b_4 of the separator, is heated by a steam-coil,

passes through overflow f_4 into b_3, and thus gradually through b, f, z, and v into still A, getting constantly hotter on its way. CO_2 and H_2S are already given off in b_3 and b_4, and more so in b_2 and b_1, where some ammonia is also set free, which, however, is retained in the upper, cooler chambers, whilst CO_2 and H_2S escape in the gaseous form. When escaping at m they contain but little NH_3, which is retained in W, and in case of need subsequently by a sulphuric-acid washer. The chambers b are

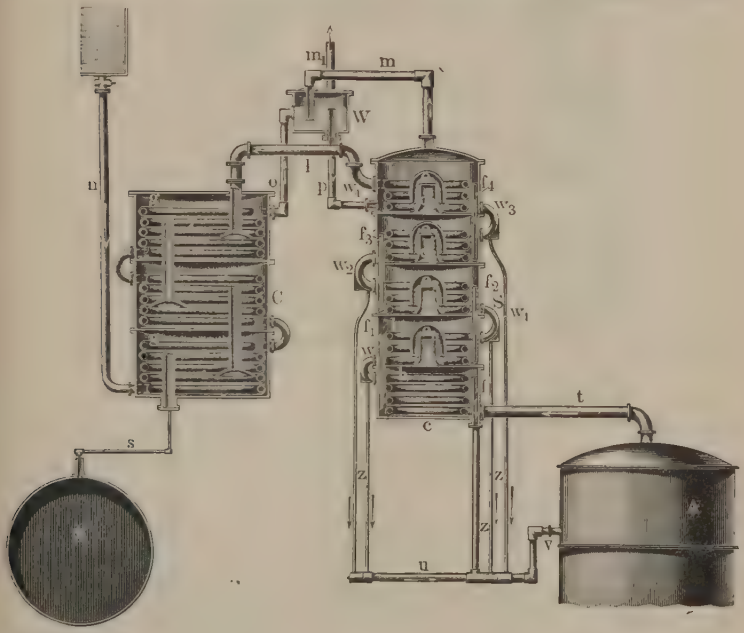


FIG. 259.

made of cast-iron, the steam coils of lead. This apparatus can be employed for making concentrated gas-liquor or else liquor ammoniæ (but the latter certainly not of *pure* quality!).

Feldmann (B. P. 10501, of 1897) also removes CO_2 and HS_2 without the employment of lime.

The apparatus of the firm, Julius Pintsch Aktien-Gesellschaft, of Berlin, is protected by Ger. P. 178030. Figs. 260 to 262 show their apparatus. The lower part of it is a heating-

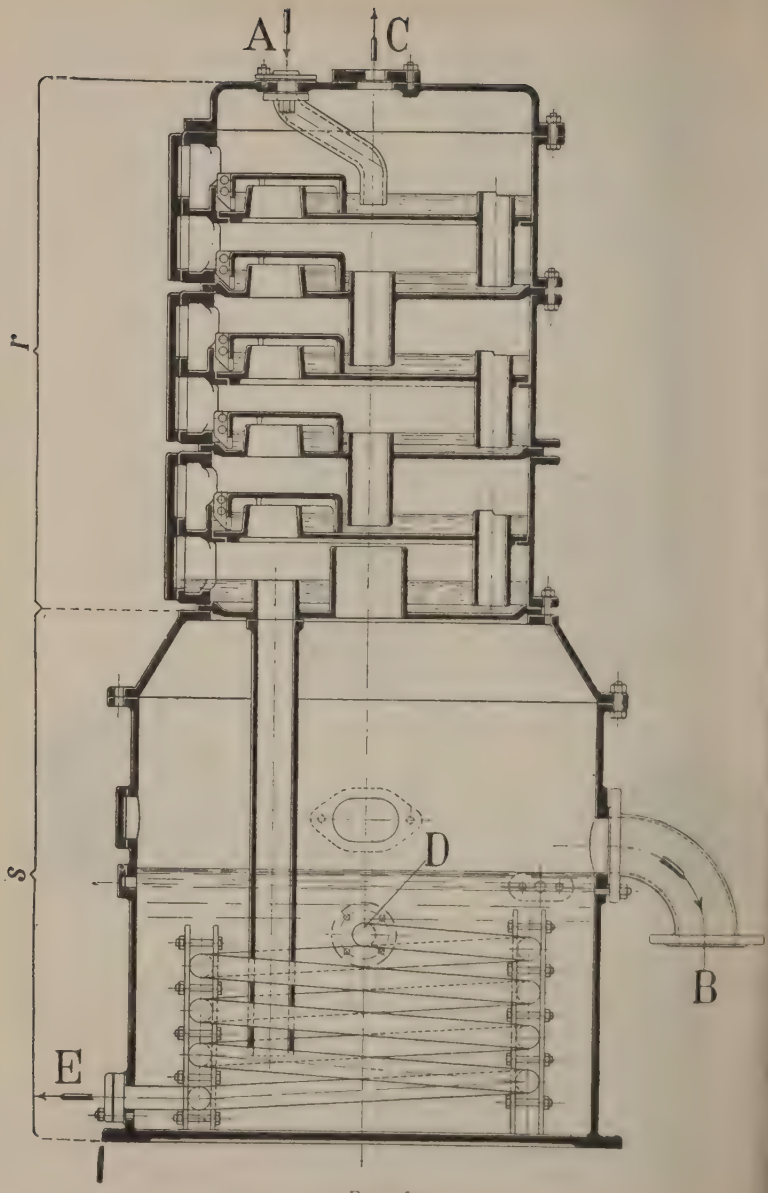


FIG. 260.

chamber, *s*, of which Fig. 261 gives a horizontal section; the upper part, *r*, is the ammonia-catcher, of which Fig. 262 gives the horizontal section (this is just alike their ammonia column-still). In the heating-chamber we see the steam entering at D and passing through a worm, the condensed water issuing at E. The crude gas-liquor runs from the store-tank through the

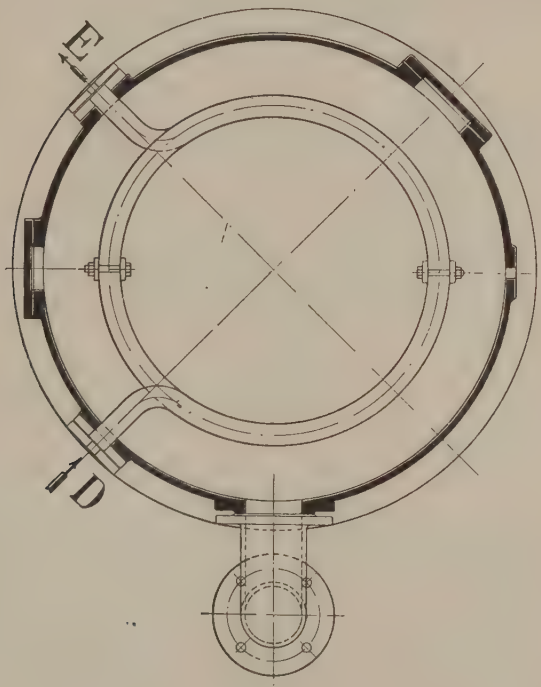


FIG. 261.

ordinary regulating-apparatus into the top chamber of the ammonia-catcher *r*, descends through it from chamber to chamber, and ultimately nearly to the bottom of the heater *s*, where it is by means of the steam-worm heated up to about 90° C. Here most of the CO_2 and H_2S, with traces of NH_3, are driven off, and rise upwards through the crude liquor flowing downwards in *r*. The NH_3 is retained here, the CO_2

and H_2S escape through C. The liquor, deprived of these gases, runs out through B, and is taken to the ammonia, still. This apparatus can be also combined with a preheater, utilizing

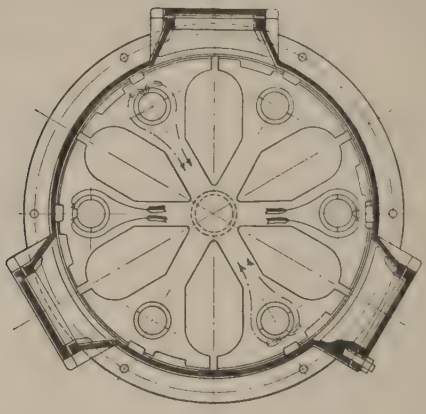


Fig. 262.

the hot waste liquor of the still for heating up the raw liquor before entering into *s*.

Solid Ammonia.

This is the name given by the Chemische Fabrik Bettenhausen, Marquart & Schulz (Ger. P. 124976, of 1901), to a mixture of 3 to 5 parts sodium stearate, dissolved in 10 parts aqueous liquor ammoniæ, or else in 80 per cent. spirit-of-wine, made at 40° C. with 85 to 90 parts liquor ammoniæ of 25 to 33 per cent. NH_3. This mixture has a consistency nearly like that of solid paraffin; already on lying in the air, more quickly when gently heated, it gives up the whole of its NH_3, leaving only the sodium stearate behind.

Carriage of Liquor Ammoniæ.

Where the distance is not considerable or small quantities are concerned, this is generally effected in glass carboys. The carboys should not be quite full, and must be kept in a cool place, lest they should be cracked by pressure of gas.

They must be very tightly corked to prevent loss of ammonia by evaporation, which can be hardly altogether avoided when the liquor is kept in stock for some time. For large quantities wrought-iron drums or tank-wagons are employed, which, however, give rise to red precipitates of iron oxides, and hence can only be employed for the crude article. The purer article is sent out in tinned iron drums. Sometimes "galvanized" iron drums are used; but it would seem that the zinc coating is gradually dissolved by the ammonia, especially if any air can enter.

Pennock and Morton (*J. Amer. Chem. Soc.*, 1902, p. 377; *Chem. Centr.*, 1902, i., 1180) have established the following facts concerning *the action of ammonia on iron.* If the iron be *completely* free from rust, concentrated ammonia not merely has no action on it, but even prevents the formation of rust, since this takes place only in the presence of *free* carbonic acid. When, however, concentrated ammonia is in contact with iron, partially covered with fresh rust, the rusting-process is promoted. If the iron be *completely* covered with a layer of rust, it is no more acted upon by concentrated ammonia.

The Board of Trade prescriptions for the carriage of liquor ammoniæ are quoted later on, p. 1014.

Testing of Liquor Ammoniæ (Caustic Ammonia).

Methods for a complete analysis of ammoniacal liquor have been given in Chapter XIII., pp. 935 *et seq.* In this place we mention only the commercial tests for the liquor ammoniæ of trade.

The percentage of ammonia in this is nearly always ascertained by means of the hydrometer, for which the tables on p. 950 may serve; but it must not be overlooked that these are valid only for the temperatures stated. In lieu of the figures for specific gravity, it is usual in Germany to employ the hydrometer of Baumé or Beck, in France that of Cartier; a table given in the Appendix will permit the reduction of these degrees to specific gravities.

Technically pure liquor ammoniæ should be colourless (even when exposed to the light for some time), clear, and not smelling too much of empyreuma. Sulphides ought to be entirely absent, as shown by lead-paper. Pure liquor ammoniæ for pharmaceutical purposes ought to be free from chlorides

and cyanides (in which case, when it is neutralized by nitric acid, silver nitrate produces no opalescence), and should be almost free from empyreuma. The latter is especially perceptible on neutralizing the liquid.

Kupfferschläger[1] proposes proving the presence of tarry matters in liquor ammoniæ by the red colour which is produced by pouring a few drops of it into a test-tube containing a few cubic centimetres of colourless nitric acid diluted with a quarter of its volume of water. According to Wittstein,[2] the pink colour does not arise if the nitric acid be at once supersaturated with ammonia, but only on partial saturation, and it is destroyed by an excess of alkali. Both chemists ascribe it to the action of nitric acid on aniline, etc. Lehmann[3] many years ago made a similar observation.

H. Ost mentions[4] that *pyridine* can be detected by its smell when nearly neutralizing the ammonia. By distilling the liquid, collecting the distillate in hydrochloric acid, evaporating and extracting the residue with absolute alcohol, a solution is obtained containing but little ammonium chloride. This is removed by addition of platinum chloride, and on evaporation of the alcoholic filtrate the platinum-pyridine double chloride separates in characteristic forms.

Künzel (*Fischer's Jahresber.*, 1890, p. 468) neutralizes 100 c.c. liquor ammoniæ with dilute sulphuric acid, well cooling, adds a little caustic-soda solution, dilutes to 400 c.c., and distils off one-third during an hour. The distillate is mixed with 10 grams mercuric chloride, diluted to 400 c.c. and again distilled. The distillate ought not to require more than 2 c.c. decinormal soda (=0·00948 per cent. pyridine) before being neutral against methyl-orange.

Krauch (p. 164 of his book on the testing of chemically pure reagents) gives prescriptions for testing liquor ammoniæ.

Pennock and Morton (*J. Amer. Chem. Soc.*, 1902, p. 377; *Chem. Centr.*, 1902, i., 1181) employ the following tests for commercial liquor ammoniæ:—(1) *Carbonic acid.*—Evaporate 100 c.c. of the liquor with 5 c.c. caustic-soda solution to about 20 c.c. To this residue add 50 c.c. water and a little phenolphthaleine, cool down to 10° C., and exactly neutralize with

[1] *Bull. Soc. Chim.*, xxiii., p. 256.
[2] *Dingl. polyt. J.*, ccxiii., p. 512.
[3] *Wagner's Jahresber.*, 1864, p. 195.
[4] *Z. anal. Chem.*, xxxii.

sulphuric acid, avoiding any excess whatever of the acid. Then add 10 c.c. decinormal sulphuric acid, boil for 2 minutes, and after cooling titrate back with decinormal caustic-soda solution. (2) *Organic substances* (apart from pyridine).—Put 10 c.c. of the liquor into a 300 c.c. Erlenmeyer flask, add 20 c.c. 1/50 normal potassium pyrochromate and 50 c.c. dilute sulphuric acid (1 : 3); boil gently during 20 minutes, and, if necessary, fill up again to 50 c.c. After cooling, add an excess of 1/50 normal ammonio-ferrous sulphate and titrate back with 1/50 normal potassium permanganate, until a faint pink colour remains for some time. Add the c.c. $K_2Cr_2O_7$ and $KMnO_4$ and deduct the c.c. of ammonio-ferrous sulphate; also the quantity of $K_2Cr_2O_7$ required in a blank test. The result is stated in c.c. of 1/100 normal $K_2Cr_2O_7$ per 100 c.c. liquor ammoniæ. (3) *Pyridine.*—Neutralize 100 c.c. of the liquor, kept cold, almost completely with dilute sulphuric acid (1 : 5). Cool down to 20° C., add 1 or 2 drops of methyl-orange, and neutralize exactly with acid or alkali as may be required. Then distil the solution, and collect 70 c.c. of the distillate in a receiver containing 30 c.c. cold water. If the pyridine present does not exceed 2·5 g. per litre, the 100 c.c. present in the receiver contain all the pyridine. Cool down to 10°, add a little phenolphthalein and a solution of mercuric chloride till the colour has been discharged; then add another 4 drops of $HgCl_2$ solution. This precipitates any NH_3 still present. Phenolphthalein is reddened by NH_3, but not by pyridine. The filtrate is titrated with normal sulphuric acid and methyl-orange; 1 c.c. normal $H_2SO_4 = 0{\cdot}070$ g. pyridine.

III. Manufacture of Anhydrous Liquid Ammonia.

This substance has become a very important article of trade since the production of artificial ice by Linde's ice-machines has been generally adopted. Since it can be had cheaply, it replaces liquor ammoniæ to some extent, and is likely to do so still more where the cost of carriage is of importance.

Anhydrous liquid ammonia is manufactured precisely in the same way as liquid carbon dioxide. A special apparatus for this purpose has been patented in Austria (17th January 1897) by the Consolidated Refrigerating Company.[1]

[1] *Dingl. polyt. J.*, cclxiv., p. 620.

Gaseous ammonia is obtained from highly concentrated liquor ammoniæ by means of a vacuum-pump, and is well-dried before compression. To obtain a pure article, the liquid ammonia is several times allowed to expand in the gas-holder, which causes most impurities to remain behind in the liquid form. These impurities (water, acetone, alcohol, lubricating-oil, ammonium carbonate) impair its cold-producing functions; some of them (alcohol) seem to be the cause of occasional explosions.[1]

Strombeck (U.S. P. 477089, of 1892) purifies ammonia before compression by passing it at 90° C. over fused sodium, which retains all the above impurities, with evolution of hydrogen. The latter is removed by means of palladium sponge, which absorbs 800 times its volume of hydrogen, and of which 250 g. suffice even for a large plant. Only then gas is passed into the condenser, and furnishes a liquid of 99·995 per cent. NH_3.

The apparatus shown in Figs. 263 to 265, for the production of liquid ammonia, is supplied by the Germania Engineering Works, formerly I. Schwalbe & Son, of Chemnitz. It consists of an ammonia compressor with steel valves, placed on a box which in its upper portion holds the condensing-worm, in its lower portion a welded wrought-iron cylinder in which the liquid ammonia from the worm is collected. The cooling-water enters at the bottom and issues at the top. The gaseous ammonia aspirated by the compressor is liquefied in the worm by means of combined cooling and pressure, and runs into the cylinder, from which it is forced by a pipe, reaching to its bottom, into steel bottles, like those employed for liquid carbonic acid, holding about 20 kg.

Krebs (B. P. 17313, of 1897) gradually evolves NH_3 from aqua ammoniæ by heating, returns the vapour through the solution under treatment, separates the aqueous vapour by cooling (?), and compresses the pure NH_3 with further application of cooling.

Morris (U.S. P. 712704) describes a condenser for liquefying ammonia gas.

Frerichs (U.S. P. 586950) purifies liquid ammonia by redistillation. According to his U.S. P. 905415, he heats commercial ammonium sulphate to about 200° C., in order to volatilize

[1] Strombeck, *Fischer's Jahresber.*, 1892, p. 321.

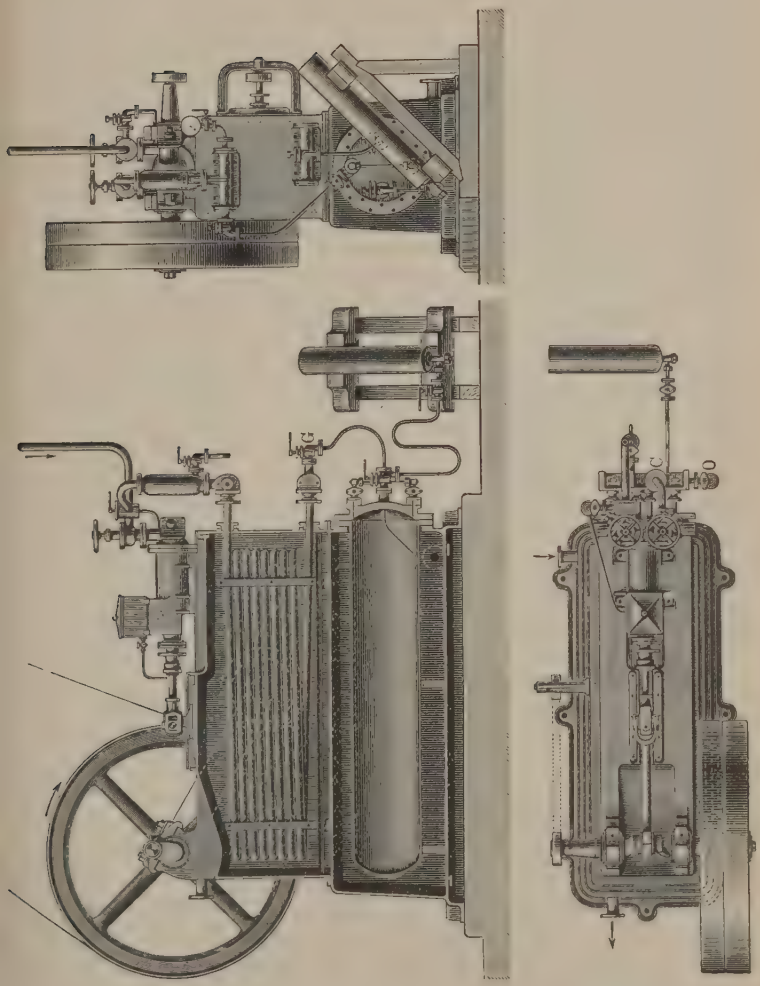


FIG. 263.

carbon compounds, blowing in air at the same time. He then raises the temperature first to 350°, then to 400°, in order to produce the reaction: $(NH_4)_2SO_4 = NH_4HSO_4 + NH_3$. The free NH_3 is collected and condensed, the ammonium pyrosulphate, formed from the acid sulphate when heating to 400°, is dissolved in water and employed for absorbing impure NH_3.

The "Bamag" Company first prepares perfectly pure ammonia gas, by the processes described on pp. 996 *et seq.* for pure liquor ammoniæ, but instead of passing it into absorbers charged with water, it is further dried by intense means, and is then passed into a gas-holder, luted with oil. From this it is pumped away and is liquefied by very strong pressure and strong cooling.

According to the rules of the German railway companies, the steel bottles for liquid ammonia must stand a pressure of 100 atmospheres, and should be tested for it once every three years. They must not contain more than 1 kg. of ammonia for each 1·86 litres capacity.

According to experiments made by A. Lange, the danger of explosion is not materially increased by the air generally contained in liquid ammonia. When heating the steel bottles, the pressure increases gradually, until the vessel is quite full; if the heating is continued, the pressure increases at first rapidly, afterwards again slowly. If filled according to the German railway rules, the bottles can be heated to 65° C. without any fear; only two-thirds of the tested pressure is then attained, and the bottles never give way unless heated above 68° C.

For *the carriage of liquid ammonia as a cargo on board ship*, the Board of Trade has issued regulations, according to which it must be packed in iron vessels, tested to a pressure of 675 lb. per square inch, and stored in a part of the ship beyond the influence of any heat from boilers or furnaces, and remote from the living quarters. The *aqueous solution of ammonia*, of sp. gr. 0·880, should be conveyed in drums of about 12 galls. capacity, with an empty space equal to 5·33 per cent. left in each drum. The drums should be capable of withstanding a pressure of 66 lb. per square inch, and should be packed in cases with no more than four drums in a case, the interstices being filled with sawdust, but for short voyages, as to Ireland or the Continent, no cases are required. The drums should not be exposed to the heat of the sun or of a fire, and should not be

covered with a black tarpaulin. Ammonia solution of sp. gr. 0·959 and upwards is exempted from these prescriptions.

Composition and Analysis of Anhydrous Liquid Ammonia.

Strombeck found in 6 samples of American liquid ammonia from 96·984 to 99·180 per cent. NH_3, 0·010 to 0·079 water, 0·117 to 1·644 "colourless liquid," 0·004 to 0·087 ammonium carbonate, 0·004 to 0·035 lubricating oil, and up to 0·007 per cent. sand, oxide of iron, etc. In the "colourless liquid" he found acetone, methyl-alcohol, ethyl-alcohol, and isopropyl-alcohol. Lange & Hertz (*Z. angew. Chem.*, 1897, p. 224) found in 20 kg. a residue of 187 c.c., consisting of water, pyridines, acetonitrile, ethyl-alcohol, ammonium carbonate, benzene and naphthalene, a little lubricating oil and solid substances (ferric oxide).

The *practical valuation* of liquid ammonia is confined to the estimation of the residue left on evaporation, without inquiring into its composition. Bunte & Eitner (*J. Gasbeleucht.*, 1897, p. 174) allow the liquid by its own pressure to enter from the steel bottle into a pipette (Fig. 266, p. 1016), and weigh the residue left on slow evaporation, after having at last heated the pipette to 70° or 80° in a current of dry air, with several caustic-potash bulbs attached. This process, as Lange & Heffter have shown (*Chem. Ind.*, 1898, p. 2), is inaccurate, since benzene, acetonitrile, alcohol, and even pyridines are carried away by the air at the ordinary temperature.

Urban (*Chem. Zeit.*, 1897, p. 720) employs a pipette (Fig. 267, p. 1016) holding about 70 c.c., 30 mm. wide, contracted below into a 5 mm. tube, 5 or 6 cm. long, divided into $\frac{1}{20}$ c.c., whilst the remainder is divided into cubic centimetres. This facilitates the measuring of the ammonia and of the residue; the specific gravity of the former can be taken = 0·617, that of the residue = 0·8, in the case of much water = 0·9.

The Linde Ice-machine Company (*Z. angew. Chem.*, 1897, p. 224) employ a glass tube, 27 mm. wide, with handle, contracted below into a tube 9 mm. wide. It holds 30 c.c. up to the place where a little hole is made in the wider tube; the narrow tube contains 3 c.c. divided into 10 parts. The apparatus is filled from the iron bottle until the liquid runs out of the side hole; it is then allowed to evaporate, and the residue read off in per cent.

Lange & Hertz (*Z. angew. Chem.*, 1897, p. 224) object to

this that the specific gravities of the liquid ammonia and the residue are not the same, that some of the latter may be mechanically carried away by quick evaporation, whilst on slow evaporation water may be condensed inside. They therefore employ a special tube, taking account of the different specific gravities (0·68 at $-38°$ C. for NH_3, 0·9 as the average of the residue). The upper part holds, up to the point 49 c.c. 33·3 g. NH_3; the narrow lower part 1·1, divided into 15 parts, each of

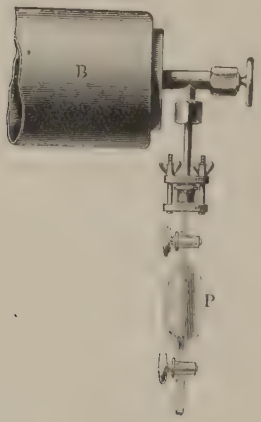


FIG. 266.

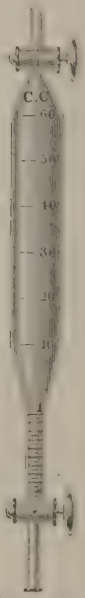


FIG. 267.

them = 0·2 per cent. The whole is left for spontaneous evaporation, a nicked cork being put in the top of the instrument. The contents of the tube boil regularly, and after three hours all is finished, or in half an hour, if the narrow part is placed in water. —An error in this method is attributable to the quantity of ammonia left in the residue (up to 25 per cent.); but there is a simple way out of all the difficulties, and for ordinary purposes the just-described method (which is much handier than any working with glass-tap pipettes) is sufficient. The manufacturers

ought to guarantee a maximum of 1 per cent. residue to be found by this method.

An apparatus for testing liquefied ammonia has been constructed by F. W. Frerichs, at St Louis (*Amer. Inst. Min. Eng.*, 28th December 1908; *G. Ind. and Eng. Chem.*, 1909, p. 362).

The analysis of anhydrous ammonia is also treated by Lucion and Paepe (*Bull. Soc. Chim. Belg.*, 1906, p. 347; *Z. angew. Chem.*, 1908, p. 497). Commercial anhydrous ammonia contains rarely as much as 99·9 per cent. NH_3, sometimes down to 97 per cent. The impurities are: methylic, ethylic, and isopropylic alcohol, acetone, acetonitrile, amines, pyridines, benzene, naphthalene, sometimes ammonium carbonate, a little lubricating oil, ferric oxide, sand, etc. The authors employ for its analysis a modification of Bunte and Eitner's method (*vide supra*, p. 1015). One hundred and sixty to 170 g. of the liquid ammonia is placed in a Kroecker bomb, and the gas issuing from this very slowly passed through three large U-tubes, containing caustic soda, into a measured quantity of seminormal sulphuric acid, contained in two bottles of 3·5 l. capacity, placed in succession and connected in such manner that the acid cannot get back. In the end dry air, free from CO_2, is passed through the apparatus and the bomb is heated on a water-bath for half an hour. The carbon dioxide present is estimated in another sample by absorption in aqueous NaOH solution.

IV. Manufacture of Sulphate of Ammonia.

Most of the ammoniacal liquor is worked for this article, which is easily carried, and is saleable almost in any quantity for agricultural purposes, in spite of the largely increasing production from coke-works, etc. Its manufacture is not so profitable as that of pure liquor ammoniæ, but the latter is only saleable in limited quantities.

The number of apparatus proposed, or even actually employed, for working gas-liquor or other ammoniacal liquors is very great; a complete enumeration of them would not serve any useful purpose, and will not even be attempted in this treatise. Many of them are more or less unsuitable or quite obsolete.

Most of the apparatus mentioned below serve only for the

production of sulphate of ammonia, but some of them answer equally well for preparing from gas-liquor, etc., a concentrated crude solution of ammonium carbonate and sulphide, for the use of ammonia-soda works or any other purpose, in order to save the comparatively excessive carriage on the ordinary dilute gas-liquor. Some of them are also intended for making liquor ammoniæ, but this is best done by special apparatus.

We shall not detain ourselves with describing the simple boilers formerly in use, sometimes along with a sort of imperfect dephlegmating apparatus, but shall at once proceed to the description of apparatus more calculated to save fuel and labour. We begin with the most simple apparatus; after these we shall describe the more perfect continuously working stills, which seem likely to be extensively used in the future (*cf.* Fletcher, *Industries*, 1890, p. 37).

Coffey Still.

We shall first, in Fig. 268, give a sketch of the combination of apparatus employed at a London works, where 100,000 gallons of gas-liquor are worked up per day, representing the product of 600,000 tons of coal per annum. The liquor arrives in canal-boats, A, and is pumped up by the pump *a* into a large settling-tank, B, where it remains for 24 hours. It is then pumped by the donkey-pump *b* into a "Coffey" still, C, 30 feet high, 12 feet long, and 5 feet wide, into which steam of 2 atmospheric pressures is blown by 5 tubes. Here the volatile ammonium compounds are separated from the water and the non-volatile salts, which are usually run away into the canal because they contain only 3·5 per cent. of the NH_3, and do not pay for working off with lime. [This is a contention frequently made, but probably quite erroneous.]

The volatile ammonium compounds pass out of the top of the still through a 2½-inch worm, perforated with numerous ½-inch holes, into the cylindrical saturator D, made of strong lead (20 lb. per superficial foot), the lower two-thirds being strengthened by strong planks bound with iron hoops. It is 6 feet high and 10 feet wide, and is filled two-thirds of its height by means of the funnel-tap *d*, with a mixture of equal parts of sulphuric acid (preferably "brimstone acid") of 140° Tw. and water, which remains in the apparatus till it is

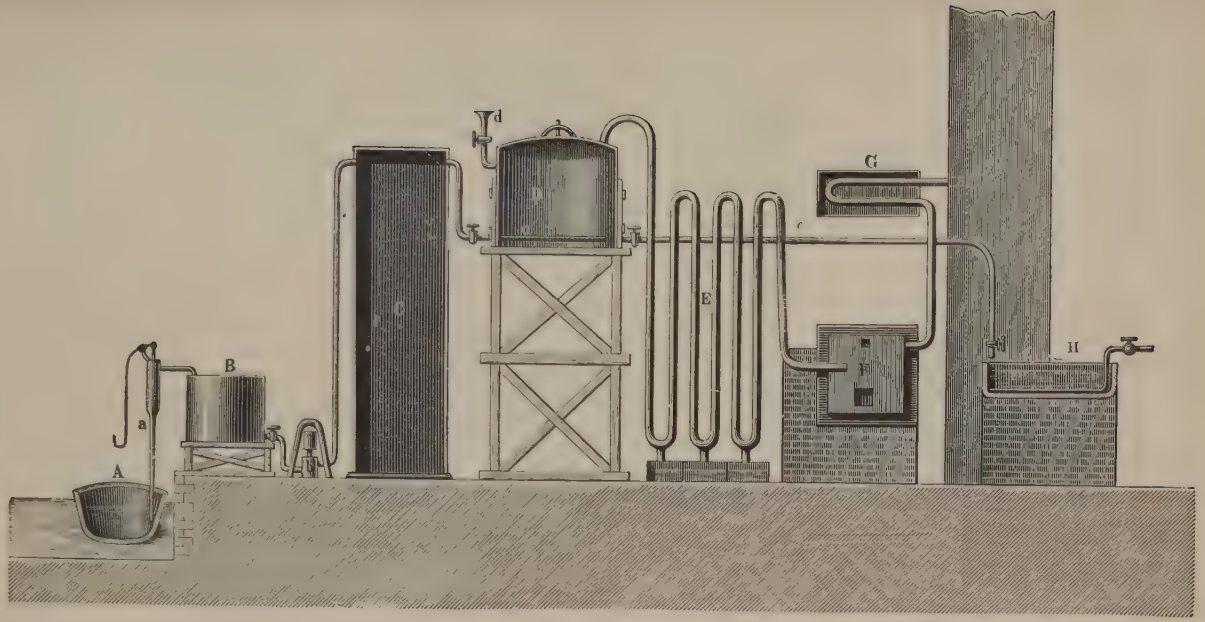


FIG. 268.

completely saturated. The acid is purposely diluted, to prevent the salt from crystallizing within the saturator. When the saturation is completed — the liquor showing only a very faint acid reaction—steam is blown through for a quarter of an hour, to drive off all the sulphuretted hydrogen. The vapours evolved in this process and during the whole operation pass through the air-condenser E, to condense the moisture which is carried along, and then through a 7-inch metal pipe into the burner F. This is a square brickwork chamber, about 5 feet wide, 8 feet long, and 4 feet high, loosely packed with firebricks, which are made red-hot before the commencement of the operation. Here the hydrogen sulphide takes fire, and is kept burning afterwards by its own heat. The hot gases pass through a steam-boiler (indicated at G), where their heat is partly utilized, and thence into a chimney, in which no smell at all of hydrogen sulphide can be perceived [but what becomes of the sulphur dioxide formed?]. The solution of salt is run from D through the pipe *e* into the lead pans H, 8 feet in diameter, 2 feet deep, made of 20 lb. leads heated by a steam-coil working at two atmospheric pressures. There is no smell perceived here. The ammonium sulphate crystallizing is fished out with a wooden spade, washed a little, and drained on a wooden floor. The mother-liquor serves for diluting the acid in the saturator. This process (*i.e.*, saturating with dilute acid and evaporating the solution) is preferred to the continuous running-in of acid and fishing-out of salts, because the result is superior. [This perfectly agrees with the statement quoted (p. 990) from Watson Smith.]

Coffey's still was originally constructed for rectifying spirit-of-wine, but has been employed for many similar purposes—for ammonia first by Newton, in 1841. Fig. 269 represents the shape employed for spirit-of-wine: that employed for ammonia is essentially the same; but wood lined with lead is substituted for copper. It consists of an oblong vessel, B, and two superposed columns, CDEF and GHIK. The former is called the analyzer, the latter the rectifier. The whole is made of 6-inch wood lined with lead, so that little heat is lost by radiation. B is divided into two chambers, B′B″, by the horizontal diaphragm *d*, which is perforated with numerous apertures for the passage of the vapour, and is, moreover, furnished with several

valves opening upwards, *e e*, in case of more vapour being given off than can escape through the apertures. A pipe, *v*, reaches

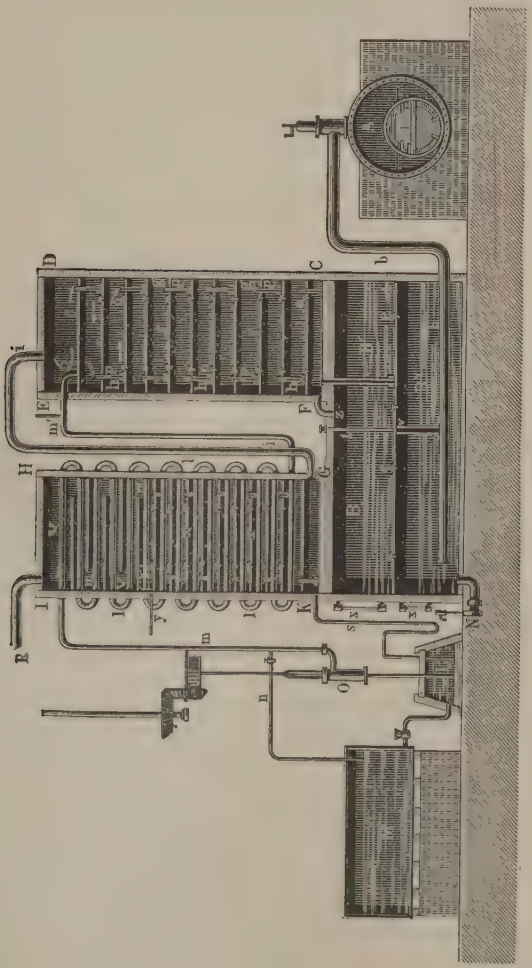


FIG. 269.

nearly to the bottom of B″, where it dips into a hydraulic lute; it can be opened or shut off by a valve attached to the rod *t*, which passes through a stuffing-box at the top. *x x* are liquor-

gauges for B′ and B″. The *analyzer* CDEF is divided into 12 chambers, *f f f*, by sheet-iron diaphragms, *g h*; these also contain many perforations, as well as valves opening upwards, *o o*; also overflow-pipes, *p*, projecting about an inch above each plate, so that a corresponding depth of liquid always remains on each diaphragm. The pipes *p* reach down to the next lower diaphragm, where they dip into hydraulic lutes (traps), so that no steam can escape through them; they are inserted at alternate ends of the diaphragms.

The *rectifying-column* GHIK is in a similar manner divided into 15 chambers. The lower ten of these are filled exactly like those of the analyzer, their diaphragms being furnished with perforations, valves, and overflow-pipes. The top chamber of these ten is covered by a metallic diaphragm, with only one large opening at *w* for the passage of vapour, and an overflow-pipe *s*. *w* is surrounded by an upright flange, which prevents the return of the most rectified liquid into the lower part of the column. *s* is closed by a hydraulic trap of much greater depth than the others, from which a pipe, *y*, carries away the condensed but still very hot liquid into a worm or other refrigerator.[1] The upper five chambers, *v*, are formed by plain unperforated diaphragms, with openings at alternate ends large enough for the passage of both vapours and liquid; their only use is to cause the vapour to pass along the pipe *m* in a zigzag direction, so as to enlarge the cooling-surface. The pipe *m* runs through all the 15 chambers in a zigzag, as shown in Fig. 270, the bends *l l* (Fig. 269) forming the connection between the pipes of the different chambers, thus constituting one continuous pipe, leading from the pump O upwards, then downwards through all the chambers of the rectifier, again rising upwards outside, and finally ending in the analyzer at *n′*. M is the store-tank for the liquid to be rectified; L, the well for the pump O, which is working continuously, and supplies rather more liquor than is necessary to keep the apparatus going; the surplus runs back into M through a pipe, *n*, furnished with a stop-cock by which

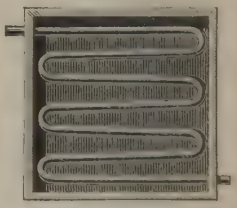


Fig. 270.

[1] This can be omitted in rectifying gas-liquor, except when liquor ammoniæ is to be made in the apparatus itself.

the operation can be exactly regulated. The necessary heat is supplied by the steam from the boiler A; the steam-pipe *b b* within the receiver B″ branches into a number of smaller perforated pipes (these are not shown in the diagram).

An operation is commenced by setting the pump O in motion, till all the zigzag pipes, *m m*, are filled and the liquor passes into the analyzer at *n′*. The pump is then stopped, and steam is let into the still through *b b*; it passes up through the receivers B″ B′, then through the pipe *z* into the analyzer, passes into *i*, in which it descends and enters the bottom of the rectifier at G. It then rises through the chambers X X, envelops the zigzag pipes, and heats the liquor in them. When the attendant by feeling the bends *l l* perceives that perhaps eight or ten of the chambers of the rectifier have become heated, he again sets the pump to work. The gas-liquor, now nearly boiling-hot and always in rapid motion, flows from *n′* into the analyzer and downwards in this through the overflow-pipes *p p* from chamber to chamber, as shown by arrows in the top chambers. It cannot pass down through the perforations of the diaphragms, whose number and size are so regulated that they are not more than sufficient to afford a passage for the vapours upwards when under some pressure. Steam and vapour thus pass in each chamber in numerous jets through a thin stratum of liquor, and so completely expel all volatile ammonium salts that in B no trace of these can be found. When the water-gauge *x* shows that B′ is nearly full, the valve at *t* is opened and the contents of B′ are discharged into B″. When this is also full its contents are discharged by the cock N, the contents of B′ are again run into B″; and in this way the process goes on so long as there is any liquor to be distilled. The boiling-hot spent liquor running from B′ serves to raise the temperature of the water intended for feeding the steam boiler A.

Having now followed the liquor in its course onwards to the point where it is deprived of all volatile ammonia, we will trace the course of the steam. This in its passage through the 12 chambers of the analyzer takes up a large quantity of ammonia, and is partly condensed to water. The remaining mixture of steam and vapour at *i* passes into the rectifier, envelops the pipes *m m*, heats their contents, and by condensation parts with more of its watery portion, which condenses in a boiling state

on the various diaphragms. What escapes through *w* is nearly pure ammonia; and this, after being further cooled in *v v* and having lost the last portions of water, escapes through R into the saturator D, Fig. 268.

If liquor ammoniæ is to be made, the gas-liquor must be mixed with lime. In this case less steam is blown in, so that the chambers *v v* remain at the ordinary temperature and from the pipe *y* strong liquor can be obtained at will, passing at first, by preference, through a refrigerator. The water condensing lower down in the rectifier contains a little ammonia, and hence runs back through *s* into L, in order to be pumped up again by O.

The operation is mainly regulated by observing the thermometer *m'*, which shows the temperature of the liquor issuing from *n'*. Whenever the liquor is too hot, more liquor is let into the apparatus, or *vice versâ*, which can be effected at will by the overflow-cock *n*.

According to the requirements of certain works, Coffey stills are made more or less wide and high, with a corresponding number of steam-pipes and chambers. Such stills hardly pay when less than 10,000 gallons of liquor are worked up per day.

Sometimes they are made much less elaborate than is shown in the above description, plain shelves (up to 60 in number) springing from opposite sides of the tower, and being so made as to retain upon them a thin layer of liquor, the excess of which runs over the free edge of one partition to the next partition below it, and so on to the bottom. Something like this has been patented by Brullé and Leclerc (B. P. 1086, of 1880).

At one ammonia-works the Coffey stills are from 18 to 25 feet high, 6 to 10 feet long, and 1 or 2 feet wide, with 20 or 30 diaphragms, 3 inches apart; at the top there is a space of 6 inches, at the bottom another of 2 feet (in lieu of the receiver B, Fig. 269). Steam of 1½ to 2 atmospheres is employed. The liquor used in this works is 7½° Tw. strong; the solution of ammonium sulphate is boiled down to 52 Tw. before it is allowed to crystallize.

Horizontal Cylindrical Stills.

At another ammonia-works the gas-liquor is distilled in *horizontal cylindrical stills*, A (Fig. 271), holding 10,000 gallons,

and charged with 7000 gallons each time. The heat is applied by somewhat superheated steam in a closed coil. It is preferable to employ gas-liquor of not less than 5° Tw., or, say,

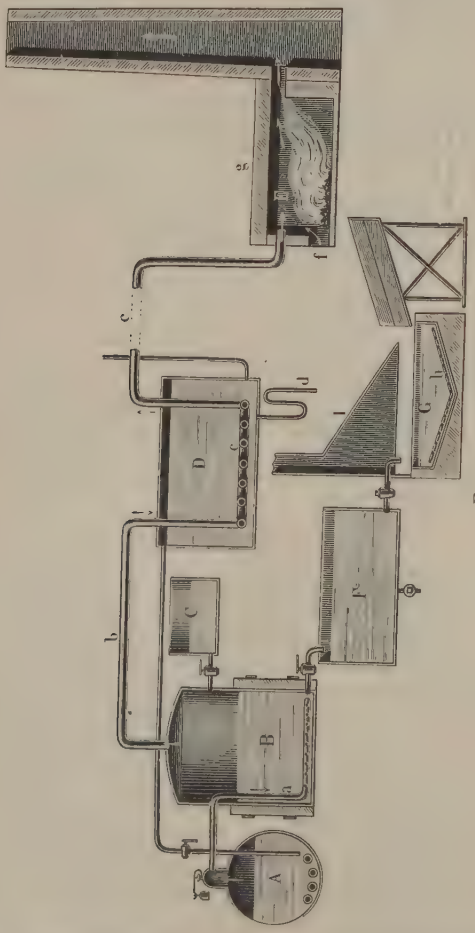


FIG. 271.

10 ounces, without addition of lime. Experience has shown that the loss, including the fixed ammonia, is always 1 ounce per gallon; so that from a 16-ounce liquor, sulphate equal to 15 ounces is obtained (?). The vapours issue through a lead

coil, *a*, perforated with ¼-inch holes 6 inches apart, into a lead saturator, B, strengthened by planks and hoops. This is charged with sulphuric acid of 47° Tw. from the tank C, which is filled by means of an air-pressure apparatus (acid-egg).[1] The vapours escaping from B pass through the 8-inch pipe *b* into the closed vessel D, where they circulate in the coil *c*; the liquid condensate runs away at *d*. D is filled with gas-liquor, which is thus heated and serves for feeding A. From D the vapours issue at *e*; they are now cooled by air through travelling round the works in a pipe 300 feet long, in which nearly all the water condenses, and are at last conveyed into the furnace E, where a fire is kept up with small coal. Air enters at *f*; and the combustion of the hydrogen sulphide is completed by causing the gases to pass along the red-hot arch *g*. The sulphur dioxide escapes into the air.

The solution of ammonium sulphate from B runs into the settler F (9 × 9 × 2 feet), and from this, through a trap 4 inches from the bottom, into the boiling-down pan G (20 feet long, 5 feet wide, 2 feet deep, half of this being straight, half conical). The heat is applied by means of the steam-coil *h*; the vapours pass away by the hood I.[2]

Continuous Saturation Apparatus.

Fig. 272 is a sketch of the apparatus in operation at a large London works, where lime is employed and where *continuous saturation* is preferred. The gas-liquor is pumped at *a* into a column, B, which it traverses from the bottom to the top in many pipes, the empty space being filled by the hot gases from the saturator A, which thus raise the temperature of the liquor. The latter now arrives in a square iron column, C, about 3 × 3 × 20 feet, packed with retort-graphite. In this the gas-liquor descends, whilst steam enters through *a'* and expels the volatile ammonium salts, which escape at *b*. The liquor passes into D, a small reservoir intended to feed the horizontal still E, in which it is mixed with lime; the steam let into this effects

[1] *Cf.* Lunge's *Manufacture of Sulphuric Acid and Alkali*, vol. i, 3rd edition, pp. 607 *et seq.*

[2] An exact description and diagrams of the steam concentrating-pan, merely sketched here, is given in Lunge's *Manufacture of Sulphuric Acid and Alkali*, 3rd edition, vol i., pp. 828 *et seq.*

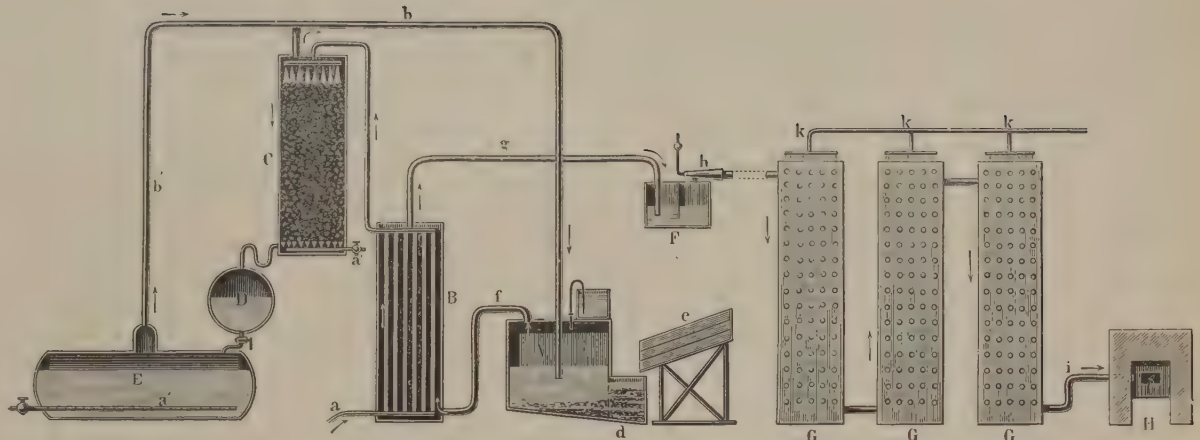


FIG. 272.

both the agitation and the distillation. The vapours escape at *b'* and unite with those from *b* before passing into the saturator A. This is a large lead vessel, continually fed with a thin jet of sulphuric acid of 140° Tw. It is adjoined by the box *d*, open at the top; the partition does not reach quite to the bottom, but is always kept luted by liquid. The sulphate of ammonia at once separates in a solid form, is raked out on the sloping bottom of A into *d*, fished out with perforated spades, and drained on the drainer *e*. The mother liquor always runs back into A; the drained salt is at once sent into the market. The hot mixture of steam and gases, escaping from A, first passes through *f* into B in order to heat the gas-liquor (as mentioned above), then through *g* into a vessel, F, where it is forced through water by a Körting's blower, *h*, and is thus washed and cooled. The complete cooling and condensation of the steam, which would otherwise be a drawback in burning the hydrogen sulphide, is effected in the columns G G G, pierced by numerous pipes, passing right across, so that abundant air-cooling takes place; and the liquid can run off below. In summer cold water is run upon these columns from the pipes *k k k*. The cool and dry gas is conveyed by *i* into the furnace H, where it passes through a coke fire, with access of air, and where H_2S is burned into SO_2, as in the former case.

This apparatus seems to be one of the best of the older forms. Each set as described is equal to the production of 100 tons sulphate per week. Recently the burning of the hydrogen sulphide has been given up, and it is, instead, absorbed in ordinary oxide-of-iron purifiers, which, however, do not appear to give full satisfaction.

Dutch Apparatus.

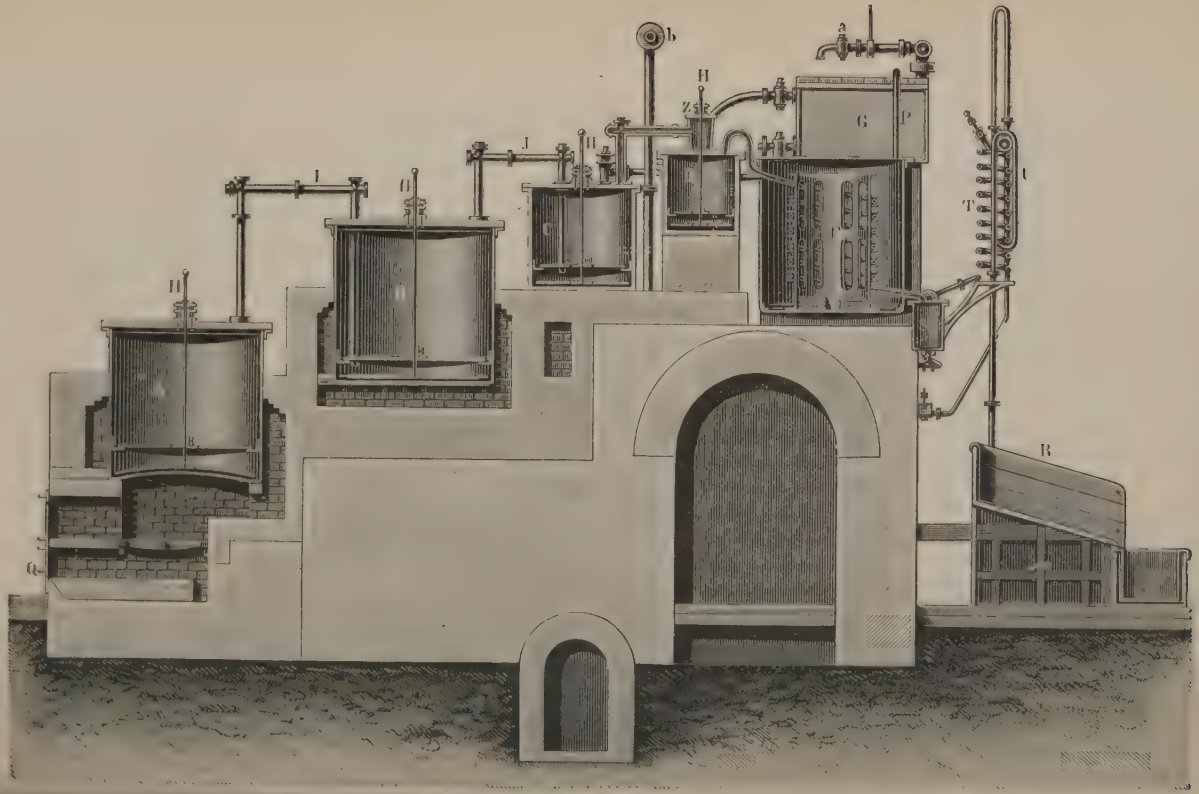
At a Dutch works I saw the following apparatus:—Three horizontal cylindrical boilers are worked in a set. The first two of these receive milk-of-lime, but this is only pumped in after most of the volatile ammonia has been expelled. The gases and steam pass through the third boiler and then into the saturator, which is of the usual form. The hydrogen sulphide and other noxious gases, given off in the closed part of the saturator, are conducted away in a pipe and are cooled down, first by cold ammoniacal liquor, then by cold water, whereupon

they are passed into a small coke fire, above the grate, in order to be burned. The whole saturator, including the open part, is covered by a large wooden hood, from which a pipe leads to the high chimney, so that there is no stench even from the open part of the saturator. The acid used is = 60° Baumé (sp. gr. 1·71), and the fished-out salt is dried on iron plates, heated from beneath.

Apparatus of A. Mallet.

This apparatus was constructed as early as 1841, but a number of them were still at work at the time of my visit at the ammonia-works belonging to the Paris Gas Company, which proves that it must be one of the most serviceable forms of the older type of ammonia-stills. It is represented in Fig. 273 in longitudinal section, in Fig. 274 half seen from above, half ground-plan, in Fig. 275 back elevation. It consists of two similar sets each of 3 stills, A, B, and C, holding above 1000 gallons apiece, A and B being heated by direct fire. They are provided with agitating-gear, H H, passing through glands in the covers, for mixing the gas-liquor and lime and for preventing any burning on. C serves for washing the vapours from B, and is at the same time heated by these. From D the vapours enter a worm, about 70 or 80 feet long, placed in the tank F and cooled by gas-liquor. The liquid here condensed flows into S, and thence into the collector Y. The gases leave the upper part of S and pass through an air-cooled worm, T, the pipes U (provided with a safety-apparatus), and into the absorbing-vessel V. The products condensed in T run back into Y.

The gas-liquor, freed from tar, is drawn through the tap *a* into the measuring-vessel G, which at the bottom is connected by a tap with the cooler F; a pipe, branching off at the top, leads to the milk-of-lime pan E. The vessels A, B, C, D are connected at the bottom by the pipes K, L, N, and at the top by the pipes I, J, which reach nearly down to the bottom of B and C. The pipe M takes the milk-of-lime from E into B. Through the pipe O the contents of the vessel Y can be emptied into the vessel D. The pipe P carries to G the vapours given off in the cooler F. Z is a three-way cock, by which the pipes connected with D can be alternately put into communication. In Q is the fire, which first travels round A


b
H
G
P
T
R
Q

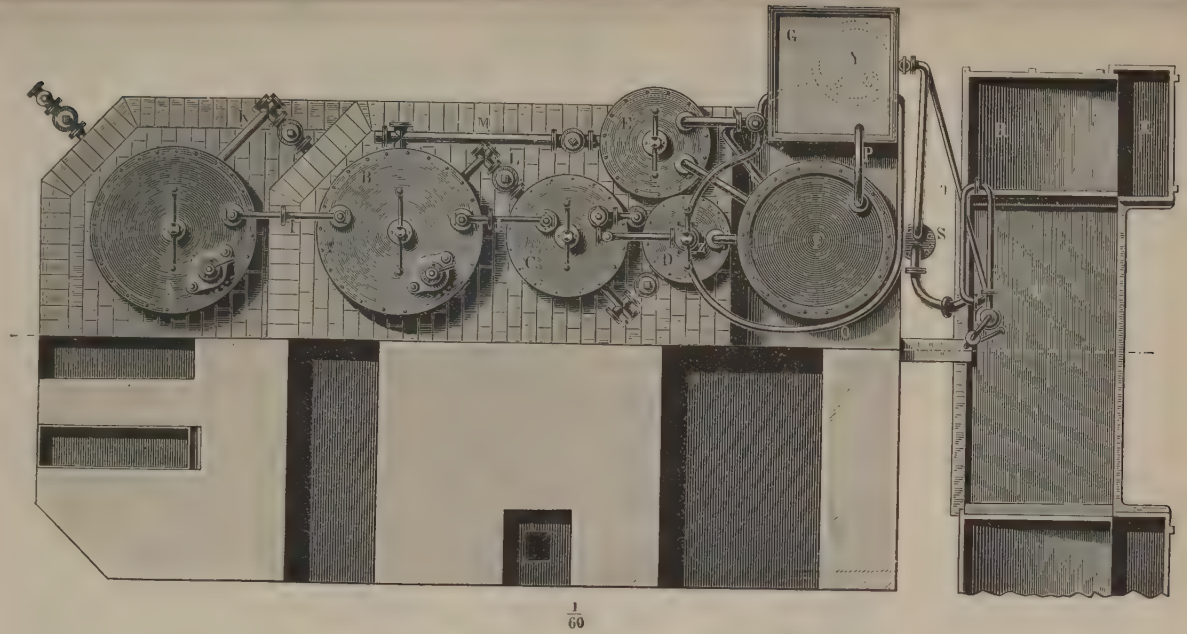


FIG. 274.

and then underneath B. R R are lead-covered wooden drainers for the ammonia-salts. X is a leaden tank for the mother-liquors, which go back to V.

The saturators are usually made of wood and lined with lead; the ammonia-gas issues through a horizontal lead pipe, lying at their bottom, into the acid or the water. The saturator has an air-tight cover; and the non-condensed gases escape

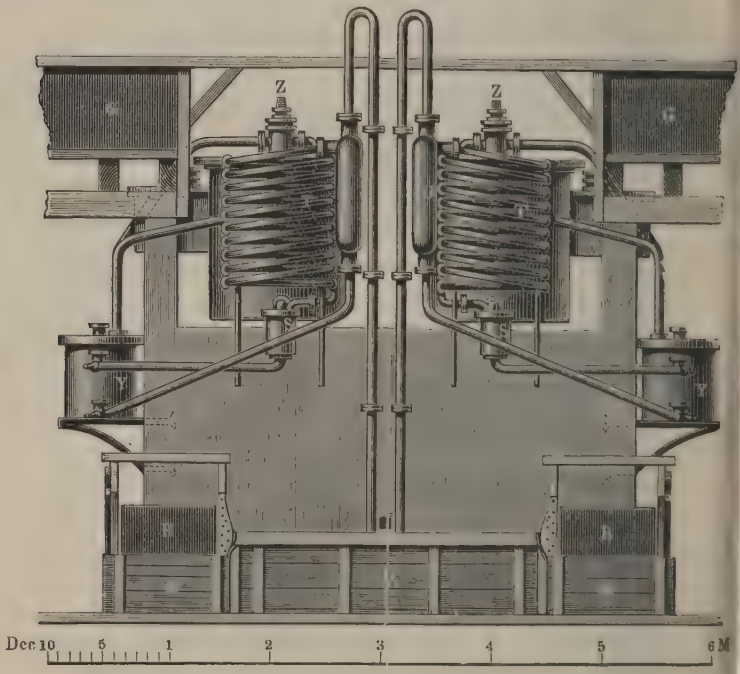


FIG. 275.

through a pipe into the fireplace of a steam-boiler, in order to be burned.

If caustic ammonia is to be prepared, before distillation a quantity of lime sufficient for decomposing all the ammonium salts must, of course, be put into the still, to avoid contamination of the product [but this cannot be effected by the employment of lime alone!]. For making ammonium chloride or sulphate much less lime is required; and sometimes none at all is

employed, the small quantity of fixed ammonium salts being given up as lost. The liquor ammoniæ is only of the crude amber-coloured quality.

In actual practice[1] only a small portion of the gas-liquor in E is mixed with lime, half an hour before the operation; most of the liquor is run from G into F, where it serves as a refrigerant and is itself heated in the process; for this purpose it enters the vessel at the bottom and leaves it at the top. The stills are provided with safety-valves and water-gauges. At the end of the process the liquid is run away into a main drain.

The worm in F is 2 ins. wide and has nine coils. The worm T, when, instead of liquid ammonia, sulphate is made, is replaced by a cylinder 10 ft. high and 4 ft. 6 ins. wide, into which the gas-delivery pipe from S enters and passes down nearly to the bottom. This cylinder is kept about one-third filled by means of an overflow-pipe shaped like an inverted siphon; the overflowing liquid is collected in Y, like that coming from S. From that cylinder the gas passes first through an iron pipe, provided with a Welter's safety-tube to prevent any liquid from being forced back by atmospheric pressure, and then into a large lead tank, into which it issues from two lead pipes, lying at the bottom and perforated by many holes. The tank is two-thirds filled with sulphuric acid of 53° B. = 116° Tw.,[2] and provided with a roof-shaped cover, from which the escaping gases (carbon dioxide and hydrogen sulphide) are carried into the chimney by means of a wood conduit. The sulphate crystallizing out is fished out from time to time, drained on sloping lead plates, and dried in a stove or upon metal plates heated by some waste heat.

As soon as a sufficient quantity of liquid has collected by condensation in the vessels Y (say once an hour), the three-way cock Z is for some minutes adjusted so that the gas from D passes no longer into the worm F, but into Y (this is best seen from Figs. 273 and 274). Its pressure forces the liquid from Y through O into D; so that no pump is needed for this. The pipe O must reach down to the bottom of Y. Every 3

[1] The following details are hitherto unpublished observations of the process as actually carried out at La Villette, Paris.

[2] When such acid is employed, the temperature of the entering gas must be 80° if the sulphate is to crystallize out continuously.

hours the contents of A are run off, and those of the succeeding stills B, C, and D run a stage lower down.

Each apparatus is charged with 12 hl. (say 270 galls.) of liquor, and 6 operations are made in 24 hours, with an expenditure of about 12 hl. of coke as fuel in 24 hours, and of 130 l. of slaked lime for each charge of 1200 l. of liquor. Each cubic metre (or ton) of gas-liquor of 3°·5 Baumé (=8°·5 Tw.) yields 70 kg. of sulphate; each apparatus yields, therefore, about 500 kg. of sulphate per 24 hours.

At La Villette at the time of my visit a daily quantity of 10 tons ammonium sulphate was manufactured in 10 double Mallet's apparatus, and 5 tons liquor ammoniæ in 4 apparatus.

One drawback of this apparatus is, that no proper provision is made for dealing with the hydrogen sulphide; it also contains a number of unnecessary complications, and is undoubtedly inferior to the modern steam-stills of Grüneberg and Feldmann.

A. Mallet later on improved his apparatus by replacing the worm-condensers by upright tubular condensers, similar to those shown in the benzol rectifying-apparatus, Figs. 177 and 184 (pp. 711 and 726), and by the addition of a rectifying-column, similar in principle to those in use for spirit-of-wine, etc. *Cf.* also p. 1047.

Grüneberg's Apparatus.

For the general principles of this, we refer to pp. 978 *et seq.*, where his apparatus for concentrated gas-liquor is described.

The apparatus, Fig. 276 (p. 1035), serves for producing ammonium sulphate. The gaseous mixture passes through *k* and alternately through *k'* and *k''* to the saturators K' and K'', containing sulphuric acid. Considerable heat is evolved by the combination of this acid with ammonia, so as to vaporize the excess of water present in the acid [provided the latter be not much under 130° Tw.]. The vapour thus generated, together with offensive gases (CO_2, H_2S, etc.), pass along the large pipe *u* and into the vessel E, where their heat is utilized for a preliminary heating of the gas-liquor, which passes at S into a coil or set of pipes, in order to be conveyed through L into the column. From E the uncondensed gases pass through *v* into a fireplace *g*, where the offensive gases are consumed. The ammonium sulphate separated in K' and K'' is put into the drainer Y,

provided with a perforated false bottom; the mother-liquors collect in M.

The coal used averages 1 cwt. for each ton of gas-liquor

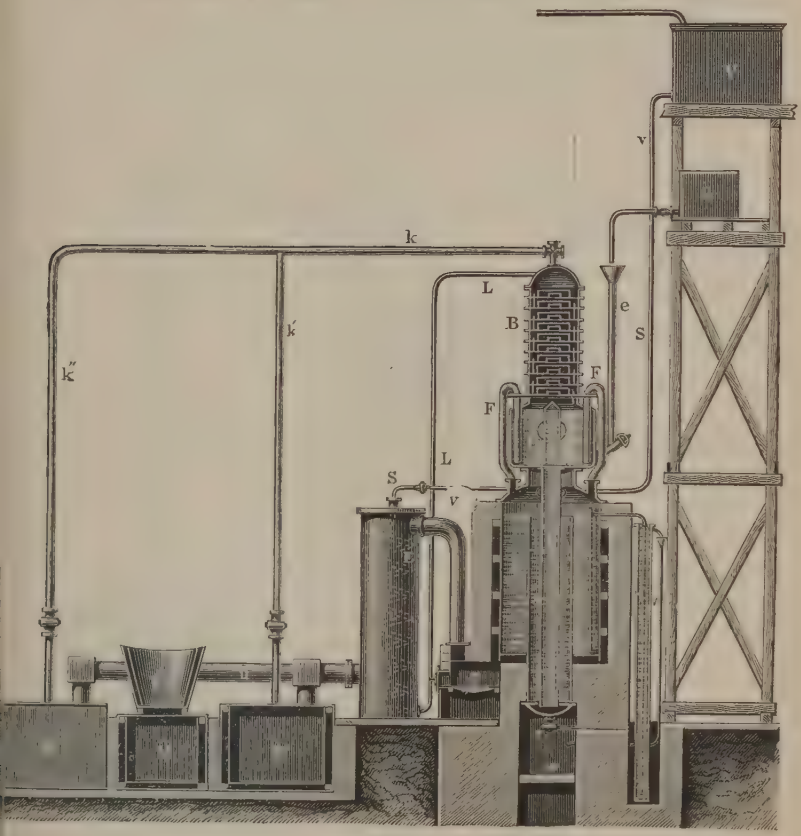


FIG. 276.

passed through the apparatus; the lime, 15 or 20 per cent. of the ammonium sulphate produced. Two men can attend to an apparatus capable of distilling 10 tons per diem. Such an apparatus, without the lime-vessel, is 10 ft. high and 5 ft. wide; the column and lime-vessel add another 8 ft. It costs from £175 to £200.

Some minor improvements of Grüneberg's apparatus are contained in the Ger. Ps. 15446 and 18852.

Practical experiences with Grüneberg's ammonia apparatus have been described by Kunath and Blum.[1]

The author owes the following further statements to the kindness of Dr Grüneberg. The two boilers A and C are now

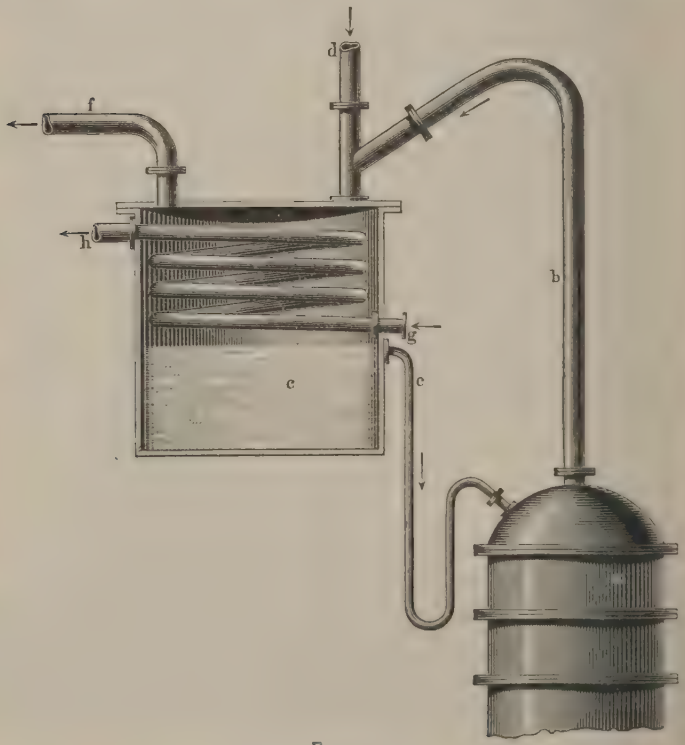


FIG. 277.

made in one piece, of cylindrical form. The lime is now introduced as sifted milk-of-lime by a membrane-pump. The milk-of-lime reservoir is an oblong iron tank with a vertical division, consisting of a fine sieve. The crude gas-liquor is now gradually heated in the following way, as shown in Fig. 277.

[1] *Wagner-Fischer's Jahresber.* for 1884, p. 311.

a is the top of the column, *b* the gas-pipe, *c* the liquor-heater; *d*, inlet for cold gas-liquor; *e*, overflow of the same and conduit into the column; *f*, outlet-pipe for the cooled gas. When heating the liquor in this way, the acid employed in the saturation must be of sp. gr. = 142° Tw. If weaker acid (106°) is to be employed, the heating of the liquor must be produced by the waste heat of the gases from the saturator, in order to have a sufficient evaporation in the same. If the object is making concentrated gas-liquor, the gases must be cooled as much as possible, and for this purpose there is on the upper part of the vessel *c* a worm, *g h*, through which cold water is constantly running.

A complete apparatus for sulphate of ammonia with lead saturator, liquor-heater, etc., for 10 tons gas-liquor costs 3500 marks (= £175). There were then more than 50 of these stills at work.

While the older Grüneberg stills are adapted to direct firing, a new modification has been patented by Grüneberg and Blum (G. P. 33320), which seems preferable in all cases where there is steam at disposal.[1] Fig. 278 shows the apparatus as adapted to the manufacture of sulphate of ammonia. In the column *a* the volatile NH_3 is expelled by steam, in B the fixed NH_3 by milk-of-lime, which is completed in C by open steam. In the saturator D the NH_3 is absorbed in sulphuric acid. The gas-liquor descends from *a* into B and C, where it is well divided by the steps, and is intimately mixed with steam, and completely deprived of NH_3; the spent liquor issues at *r*. The milk-of-lime is pumped by the hand-pump H at intervals of 10 minutes into B. The tubular heater E, heated by boiler-steam, prepares the gas-liquor before entering the column. The ammonia vapours pass through *p* into the saturator D, made of wood lined with lead, and filled with sulphuric acid, about 1·4 to 1·45 sp. gr. The inverted lead bell *g* compels the vapours to bubble through the acid. The unabsorbed gases pass through *l* into *m*, where mechanically carried-away particles of liquid are retained. The residual gases are treated in the usual manner.

The formation of sulphate is strongest below the leaden bell; it must be now and then removed by means of a wooden rake, and fished out with a copper ladle, when the liquor is

[1] English agent, Henry Simon, Manchester.

nearly saturated, which is indicated by its orange colour. The fished sulphate is drained on a leaden plate, and the drainings run back into the saturator; the sulphate is then dried in a lead-lined stove or in special machines.

If the apparatus is properly working, the steam-gauge and water-gauges must be steady, the water must run off quietly, and the acid in the saturator must well up with a gentle movement.

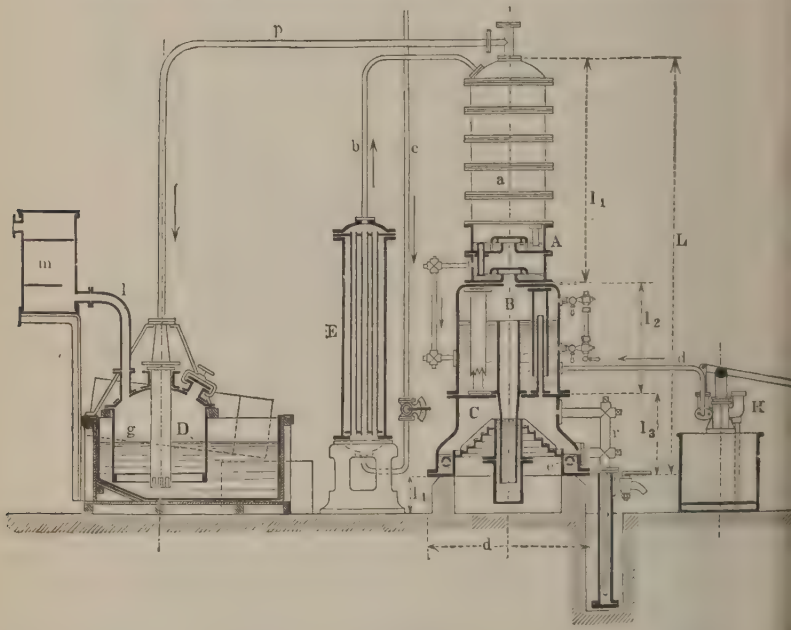


FIG. 278.

The carbonate of ammonia must by all means be driven out in the heater, since, if it gets into the lime-vessel, carbonate of lime is formed, which obstructs the apparatus. A test-cock at the bottom of the cellular heater admits of taking samples, which must be tested with chloride-of-calcium solution. If this produces a precipitate of calcium carbonate, more steam must be admitted, to complete the driving off of the ammonium carbonate. The waste liquor should not contain more than 5 parts NH_3 in 100,000. The gas-liquor must be first well purified from tarry

matters, which clog up the overflow-pipes of the column. Obstructions by carbonate of lime occur mostly in the small

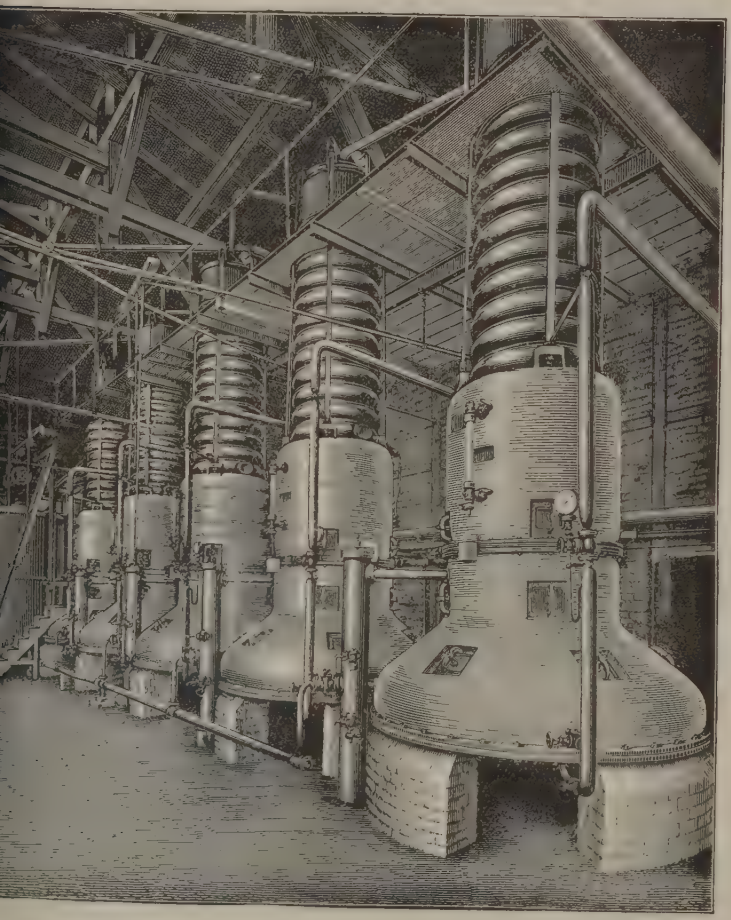


FIG. 279.

tubes within the lime-boiler; if this happens, the apparatus must be stopped, the manholes opened, and the pipes taken out to be cleaned.

Fig. 279 shows 5 Grüneberg-Blum apparatus as erected at Messrs Kunheim & Co., near Berlin, working-up together 150 tons gas-liquor in 24 hours.

These ammonia-stills are made in six different sizes, to distil from 1300 to 6600 gallons of gas-liquor per 24 hours. According to trustworthy evidence, they answered very well indeed: the ammonia left in the liquors is, on the average, not above 0·05 per cent.; there is but a small consumption of steam, very little labour, no nuisance, and no trouble.

In *J. Gasbeleucht.*, 1901, p. 895, Blum describes a pump for the milk-of-lime with automatic action.

Watson Smith gives the following calculation for distilling in a Grüneberg-Blum still the gas-liquor obtained in carbonizing 35,000 tons of coal, viz., about 35,000 tons of liquor at $5\frac{1}{2}°$ Tw.:[1]—

	Tons.	Price. s.	d.	£	s.	d.
Sulphuric acid, 142° Tw.	389	40	0	778	0	0
Lime	71	12	6	44	7	6
Labour—4 men 50 weeks, at	...	25	0	250	0	0
Coal	175	8	0	70	0	0
Casks and packing	...	...		155	12	0
Sundries, repairs, etc.	...	...		116	14	0
Depreciation of plant £300, buildings £150: total £450—at	...	10 p.c.		45	0	0
Interest on plant and buildings £450, land £100: total £550—at	...	5 p.c.		27	10	0
Gas-liquor $5\frac{1}{4}°$ Tw.	3500	12	0	2100	0	0
				£3587	3	6
Produce, sulphate of ammonia	389	£11		£4279	0	0
Deduct cost of manufacture	...	...		3587	3	6
				£691	16	6

Fig. 280 shows the apparatus for the manufacture of ammonium sulphate as fixed at the Constantia pit, in Westphalia.

Feldmann's Apparatus.

Dr A. Feldmann, of Bremen, has constructed an ammonia-still (Ger. P. 21708; B. P. 3643, of 1882; English Agents, Schwab

[1] *Industries*, 1886, p. 242.

C. T. & A.

[*To face page* 1040.

& Overhoff, Manchester), which is very much recommended, and of which very many are at work in different countries. It is a steam-still, and is adapted for making sulphate, liquor ammoniæ, or concentrated gas-liquor. Its principle is that of a continuously acting column where not merely the volatile ammonia, but also the fixed ammonia, set free by lime, is

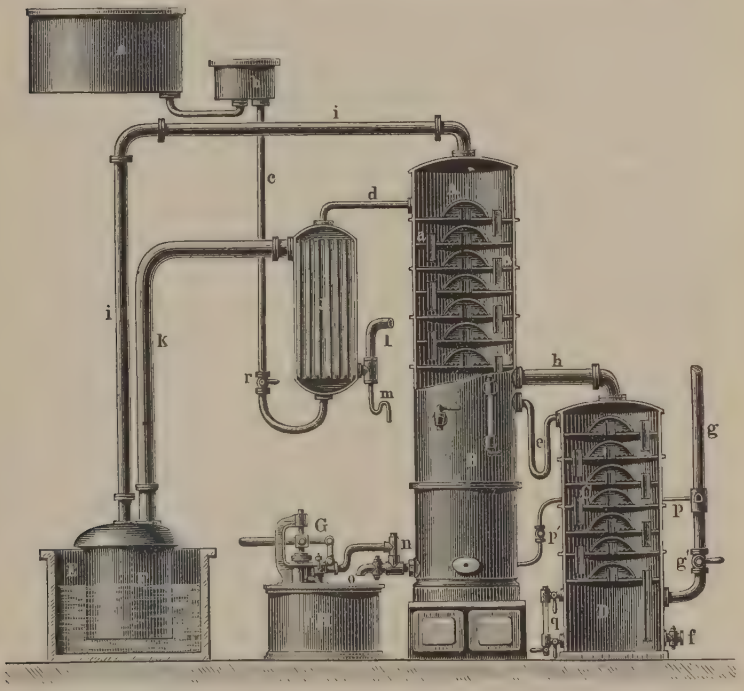


FIG. 281.

driven off. Otherwise the principle of the dephlegmation-column is the same as that adopted in the Coffey still, the Grüneberg still, and many others.

Considering its great capabilities, the apparatus requires but little room for setting up. An apparatus to distil from 8 to 10 tons of ammoniacal liquor in 24 hours occupies a space of 17 feet by 13 feet by 10 feet.

The apparatus (Fig. 281) consists of the column A, decom-

posing-tank B, and column C. The ammoniacal liquor flows from the feed-tank *a* into the supply-tank *b*, the object of which is to obtain a regular flow into the column through pipe *c* into the tubular boiler J, and thence through *d* into the top chamber of column A. From here it passes through the overflow-pipes *a* from chamber to chamber, in each of which it is boiled up by the steam which fills the stills, and is delivered free from all volatile ammoniacal compounds, through a long overflow-pipe, *a'*, almost at the bottom of the decomposing-tank B. Into this tank milk-of-lime is introduced through the pump G, and the inflowing gas-liquor is constantly mixed by a steam agitator. The inlet of steam is so regulated that the decomposed gas-liquor must run out at the top of tank B; and by the working of a sieve, introduced to break the ebullition, it passes purified and freed of surplus lime through siphon *e* into column C. In the separate chambers of this column, the ammonia formed is driven out, the spent liquor collects in the part D, and flows constantly through the tap *f*. The steam required for distilling is admitted through pipe *g* into column C; traversing the fluid in each separate chamber, it passes through pipe *h* and tank B into column A. It then rises through all the chambers in A, and leaves, charged with accumulated ammonia, by the exit-pipe *i*. Finally it arrives under the leaden bell F, which is partly submerged in sulphuric acid, contained in the lead-lined cistern E. The ammonia combines with the sulphuric acid; the gases which have not been absorbed, carbonic acid, sulphuretted hydrogen, etc., mixed with steam under the leaden bell, are conducted through the exit-pipe *k* into the cylinder J. The action of this cylinder is exactly similar to that of the economizer in Grüneberg's apparatus, so that we need not repeat its description in this place; nor need we go into the treatment of the gases. The essential difference between Feldmann's and Grüneberg's apparatus consists in this: that the former, after driving off the volatile ammonia, saturates the liquor with lime, and sends it in a *clear* state through a second column.

The usual sizes of the apparatus are for distilling 5, 10, or 15 tons of ammoniacal liquor per day; but it can be made to distil very much larger quantities. At Silvertown there is a still for 80 tons, and at Runcorn one for 200 tons liquor per day.

This apparatus (according to reliable information) easily drives off the ammonia to such an extent that the distillation test of the residues does not show more than 3 to 5 parts NH_3 in 100,000 parts of liquor; and the liberation of the NH_3 can be made practically absolute.

A very striking example of the difference between the old two-boiler system with direct firing and the rational new apparatus is afforded by a return made by the Bielefeld Corporation Gas-works. Formerly they worked only $2\frac{1}{2}$ tons liquor in a two-boiler apparatus with direct firing. The result of 100 days' working was 466 cwt. of damp, greenish sulphate, with barely 20 per cent. nitrogen. The wages per cwt. of sulphate amounted to 0·91 mark, the consumption of coke to 2·87 scheffel = 0·86 mark. After putting up a Feldmann still, the daily consumption of gas-liquor was raised to $7\frac{1}{2}$ to 8 tons; the yield of sulphate upon the coal treated in the retort was 0·9 per cent. The output of 63 days' working was 684 cwt. of nearly white sulphate, with 20·68 per cent. nitrogen. The expenses were as follows, per cwt. of sulphate:—

	Mark.
82·6 lb. sulphuric acid, 168° Tw., at 4 mark per cwt.	3·20
1·5 scheffel coke, at 0·30	0·45
Wages (at 4·24 mark per diem)	0·40
Lime	0·15
Sundries (lighting, shovels, etc.)	0·15
Amortization and interest	1·00
	5·45

Feldmann claims that his apparatus obviates the difficulty of obstructing the column by a precipitation of lime and lime-salts in a much simpler way than is done by P. Mallet (see further on); and that the employment of a column for expelling the fixed ammonia permits not merely doing this in the most perfect possible manner, but also with a minimum of steam. This is most important when utilizing the gas-liquor for manufacturing sal-ammoniac, where there should be as little subsequent evaporation as possible; but it is also very useful in making sulphate of ammonia, because it greatly facilitates the dealing with the sulphuretted hydrogen.

A more recent patent of Feldmann's (No. 71909) describes

a lime-boiler and a number of distilling cells ranged all round

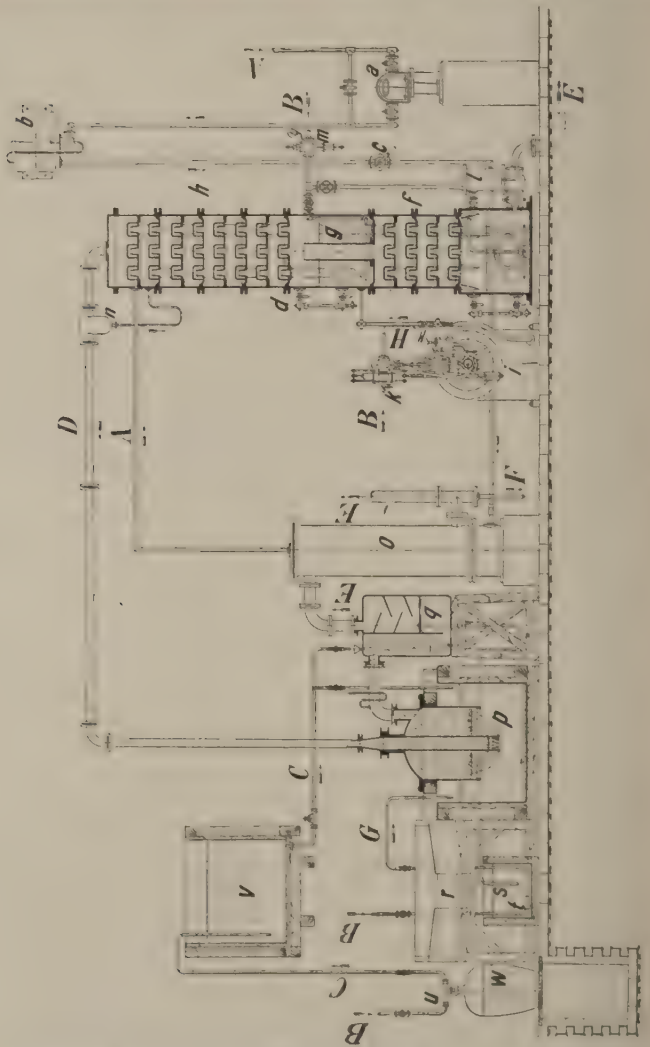


FIG. 282.

it, through which the gas-liquor runs from one to the other, and ultimately into the lime-boiler. A further patent of his

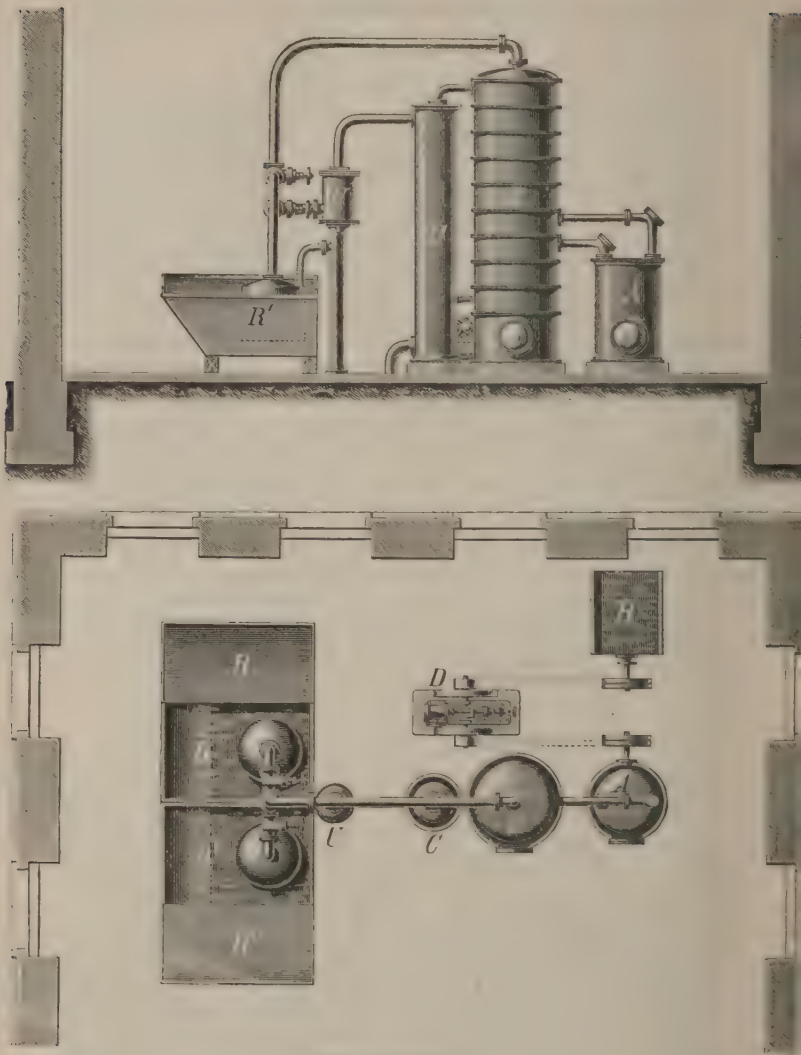
(Ger. P. 134976) describes some improvements in the saturator bell.

Apparatus of Julius Pintsch.

Fig. 282 shows the apparatus as constructed by the firm Julius Pintsch Aktien-Gesellschaft, of Berlin. The gas-liquor enters through pipe A, flows through the measuring-apparatus *a*, then through the floating-bell regulator *b*, which secures a constant height and consequently uniform supply of the liquor, through tap *c* into the preheater *o*, where it is heated up by the waste gases from the saturator *p*, and then through A into the top chamber of the column-still *h*. Descending in this, it gets into chamber *g*, where it is mixed with milk-of-lime, supplied by pump *k*, then into the lower column *f*, and leaves this through the automatically regulated outlet *l* and the escape-pipe E. The steam enters at the bottom of the column and travels in the opposite direction as the liquor, leaving the column at D and carrying all the gases into the sulphuric-acid saturator *p*. The waste cases are deprived of the last ammonia in the box *g* and from here get into the above-mentioned preheater *o*, where their heat is utilized for warming-up crude liquor. The gases escaping from here go away into the chimney, or else through an oxide-of-iron purifier for retaining the H_2S. V is a tank for sulphuric acid, into which it is forced from the store-tank *w* by the steam-jet *u*.

Apparatus of Heinrich Hirzel.

Heinrich Hirzel's column (Ger. P. 64367) is built on the same principle as that which he has constructed for liquor ammoniæ (pp. 977 *et seq.*). In Figs. 283 and 284, D is a steam-pump, by which the gas-liquor is forced into the heater C, and from this into the upper part of the column E. In this the carbonate and hydrate are expelled; about the middle of the column the liquor issues into the agitating-vessel A, where it is supplied with milk-of-lime from vessel B, and then returns into the column. The gas enters one of the two lead saturators Q or Q′, according to the position of the valves, underneath the lead bells. The gases not taken up by the acid pass through the catch-all U, to retain any acid carried away, then through the heater C, where they give up part of their heat to the gas-



FIGS. 283 and 284.

liquor traversing the heater in a coil of piping, and at last issue into the atmosphere. The sulphate is fished from Q and Q′, and drained on the slanting plates R and R′. These apparatus are built to work from 1 to 40 tons gas-liquor in 24 hours.

Improvements of Hirzel's apparatus are described in his Ger. Ps. 88953 and 91717.

P. Mallet's New Apparatus (1884).

P. Mallet[1] (*cf.* pp. 998 and 1029) has set himself the special task of making an "inobstructible column" for distilling ammoniacal liquor in contact with lime, without having to clarify it by repose (as is necessary especially for liquors produced in the treatment of sewage), or without having to relegate the lime treatment to another vessel. His apparatus is shown in Fig. 285. An ordinary column, *b b*, surmounted by an "analyzer," *a*, serves to expel the volatile ammonia. From here the liquor runs off by *c* into the apparatus (Fig. 286) intended for mixing with lime. This consists of a closed hopper, *k*, which is charged with a sufficient quantity of quicklime to serve for several hours, and of an endless screw, *l*, which conveys this lime to the mixer *m*; here it is mixed with the liquor entering at *c*, which slakes the lime, and carries it in a state of suspension through the pipe *d* into the inobstructible column. The valve *n* serves for removing from time to time unslaked pieces, stones, etc. The mixture of lime and liquor now descends the lower column *f* (Fig. 285) from plate to plate; the revolving shaft in the centre of this column, by means of scrapers fixed to it in each of the chambers of the column, keeps the lime suspended in the liquor and prevents any crusts forming on the plates. The spent liquor is cast out by the mechanical purger *h*; for very dirty lime a sludge-box must be provided, from which the deposit is taken out from time to time.

A special advantage claimed for this apparatus is that it works with quicklime and utilizes the heat of slaking, at the

[1] 52 Boulevard de la Vilette, Paris.

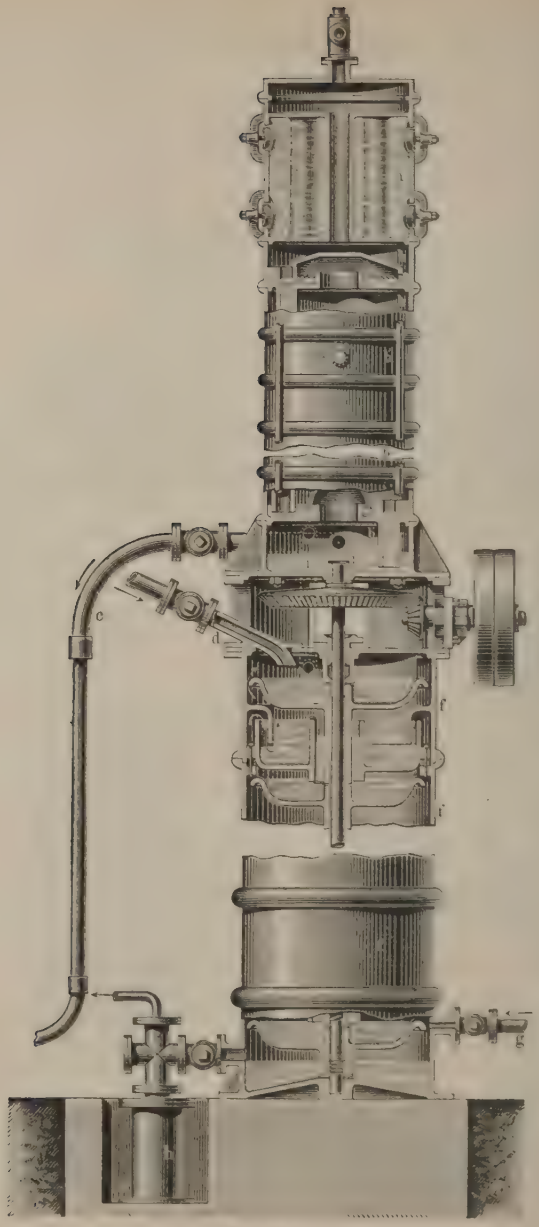


FIG. 285.

same time dispensing with the necessity of sifting the milk-of-lime; but it does not appear that this is a feature essential to the "colonne inobstruable," whose principal speciality, the revolving shaft, is evidently not without its drawbacks. Many manufacturers will prefer a simpler apparatus, dispensing with machinery.

Various forms of Ammonia-stills.

A revolving column has been patented by W. T. Walker (B. P. 16806, of 1887).

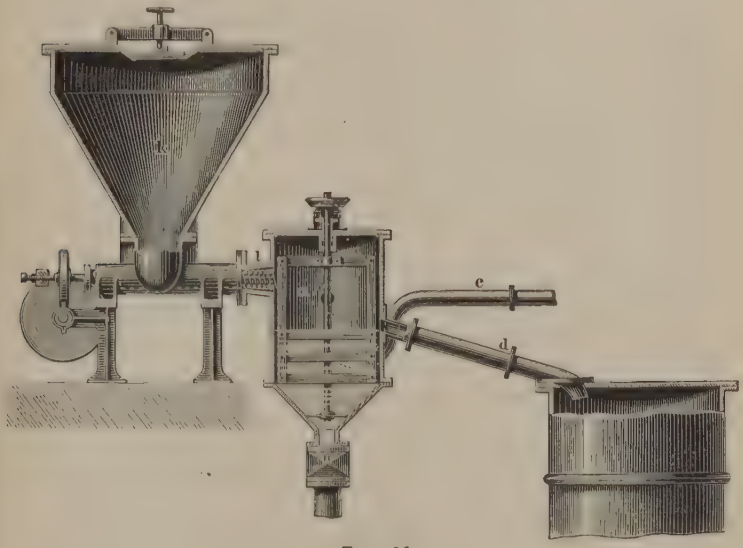


FIG. 286.

Further patents are those by Davis (B. P. 16349, of 1889); Ellis (B. P. 13003, of 1889); Holgate (B. P. 3684, of 1890); Mather (B. P. 17824, of 1892); Carr (B. P. 16978, of 1898).

Dempster (B. P. 22602, of 1893) runs the previously heated liquor into a vessel, at the bottom of which steam is injected; at the top the liquid, carried along by steam, strikes against a splash-plate, which converts it into a spray. The exhausted

liquor travels by an overflow into a second vessel, where it meets with lime.

Spence & Gilchrist (B. P. 7485, of 1893) describe special contrivances for mixing the lime with the liquid after distilling off the free ammonia.

Eckelt (*Chem. Ind.*, 1893, p. 451) describes a special overflow-pipe. Bowen (B. P. 18356, of 1889) passes heated air or oxygen through the boiling liquid, and conducts the mixture of gases and vapours given off into receivers charged with ferrous sulphate, which is thereby oxidized, the NH_3 precipitating ferric hydrate, and being converted into sulphate, and the H_2S being retained at the same time.

Outon (*Gas World*, 1905, p. 353) describes a sulphate plant, specially adapted for smaller works, but not presenting any specially new features. The same can be said of a paper by Keillor (*J. Gas Lighting*, 1903, p. 361), which is, however, interesting to gas managers by its discussion of the financial side of sulphate-making.

Francke (Ger. P. 165309) makes the steam, injected into the still, strike against blades, fixed to a movable spindle, or to the bell itself, which in this case must be movable. These blades are shaped in such manner that the liquid, rising in the still, on striking against them, favours the rotation of the bell. This arrangement causes a much better mixture of the lime with the liquid than the mere action of a steam-jet.

The same inventor later on (Ger. P. 169444) arranges the bells of a distilling-column in such manner that they can be raised or lowered from without, in order to regulate the depth to which they dip into the liquid and to facilitate the cleaning out of the column.

Adriaanse (Ger. P. 185196) provides the lower bells, attached to the agitator, with stirring blades reaching nearly down to the bottom of the shelves, so that they prevent a deposition of lime during the work and admit of cleaning out the still without opening its sides.

G. Wilton (B. P. 24832, of 1901) places on the trays of the distilling-column narrow, elongated steam openings, provided with hoods dipping into the liquid, and mud holes in the walls of the chambers opposite the end of these openings.

T. and G. Wilton (B. P. 28251, of 1902) describe a continuously

working still, especially for use in small works, consisting of superposed cylinders with movable caps in which are fitted the various connections. A furnace heats the lower chambers, either by steam or by a direct fire, and the hot gases heat the upper chambers.

The ammonia-stills of Jacob Schaefer, at Höchst, have been introduced in many places, both in Germany and abroad. They are, like many others, a combination of a lower part, where the non-volatile ammonium salts are decomposed by means of lime, with a superposed column, where the volatile salts are expelled from the liquor by the steam produced below, with a special arrangement for preheating the liquor before it enters the column. According to a report received from Mr Ernest Henss, of Nied, near Frankfort, the Schaefer stills do excellent work and are very easy to deal with.

The Société J. Jean & Cie. (Fr. P. 372171) promote the expulsion of ammonia by a finely divided current of air, employing 1400 vols. air for 1 vol. gas-liquor and a velocity of the air current of 100 feet per second. The mixture of air and vapours is hurled against large surfaces, in order to precipitate the foggy particles.

Koppers (B. P. 2399, of 1908; Ger. P. 191722) describes an ammonia still, in which the liquor flows through parallel channels, in the various chambers alternately from the centre outwards, or from the outside towards the centre.

Dill (Ger. P. 200592) patents a special shape of ammonia-stills, built up from boxes in a zigzag line, with the usual fittings of continuously working ammonia-stills, adapted to being readily exchanged for purification.

Scott (B. Ps. 3987, of 1900, and 11082, of 1901) describes various modifications of ammonia plant. So do Abendroth (U.S. Ps. 712891, of 1902, and 771031, of 1904); Osius (U.S. P. 710221, of 1902); Moore (U.S. P. 740678); Adriaanse (Fr. P. 355971); Erlenbach (Ger. P. 203309).

Ballantyne (*J. Gasbeleucht.*, 1903, p. 755) describes a "new continuous vacuum process," the plant for which is similar to ordinary ammonia plant, but is kept under a vacuum of 13 to 15 in. mercury in the still and 22 to 27 in. mercury in the saturator. The main object is a saving of fuel. (See below, under the heading "Saturators.")

G. E. Davis (B. P. 26996, of 1903) constructs ammonia-stills with serrated caps, fixed to the plates forming the tops of the chambers, so that the serrations hang free in the liquid, allowing a small rake to be inserted underneath the caps for removal of the deposit.

Holmes & Howell (B. P. 24913, 1907) in an ammonia-still in which an intermediate liming-chamber is interposed between the upper and lower chambers, facilitate the removal of sludge by making the floor of the liming-chamber dished or conical, so that the sludge tends to settle towards the outlet leading to the sludge-valve. Injectors may be placed at intervals round the chamber, so as to produce a current for preventing any settlement of the sludge near the periphery.

Obtaining Ammonium Sulphate free from Cyanides.

Grossmann (B. P. 20387, of 1905), in order to obtain ammonium sulphate free from cyanides, *without producing offensive waste liquors*, distils the gas-liquor first without lime, then boils down the remaining liquor, and adds sulphuric acid, to decompose the cyanide and sulphocyanide. The liquor now remaining behind is used over again for the absorption of ammonia. He fully discusses his process in *J. Soc. Chem. Ind.*, 1906, p. 411, whereof we give an abstract here. The principal motive for his invention was, that, even if it were possible to remove the cyanogen compounds economically, there would still be left sufficient tarry compounds and compounds of the nature of phenols, to render the final effluent noxious; and there is no method of removing these organic compounds. His own process (which at that time evidently had not yet been carried out in practical work) follows in the main line the present mode of manufacture, and branches off at a convenient point.

In the first place, the ammonia liquor is distilled by means of steam in the same stills as those used at present, but with this difference, that no lime or other alkaline substance is added.[1] The resulting liquor contains all the fixed salts of ammonia, besides tar oils and phenols and salts of sodium. When carbon-

[1] Quite a similar process is described by Thiel, in *J. Gasbeleucht.*, 1907, p. 979; cf. *supra*, p. 988.

izing 200 tons of coal per day, the total quantity of liquor leaving the still is about 10,000 gallons per day, of which 3000 gallons of water are freshly formed every 24 hours. The remaining 7000 gallons can, after cooling, be used again in the scrubbers for absorbing a further quantity of ammonia and ammonia compounds, and we shall only have to dispose of the 3000 gallons in such manner as to avoid a nuisance.

The figures given here are actual results obtained frequently in gas-works and sometimes in coke-works. In the latter, however, the quantity of water formed every day often exceeds the figures given here, as the coal used may contain 10 per cent. and more of moisture. It would be to the coke manufacturer's advantage to reduce this quantity to its lowest point by using the coal as dry as is practicable.

That portion of the liquor which goes back to the scrubbers will gradually become richer in dissolved fixed ammonia and other compounds. But it will reach its limit when that portion which is withdrawn every 24 hours for further treatment becomes of such strength that it contains as much in fixed compounds as will be equal to the total quantity of these compounds which the apparatus will produce in every 24 hours.

The quantity to be dealt with in the process would mainly depend on the quantity of moisture contained in the coal. This quantity would vary from 3000 gallons in good, dry coal to about 9000 gallons in coal containing 15 per cent. of water and 5 per cent. of other water-forming constituents.

Whatever be the quantity of liquor thus obtained, it must be evaporated to a small bulk to become amenable to further treatment. It may be generally taken that the ultimate bulk after evaporation will correspond to about $1\frac{1}{4}$ gallons for every ton of coal carbonized. It will then form a strong solution of ammonium chloride and thiosulphate, besides containing some thiocyanate, sodium chloride, and possibly some ferrocyanide. Ammonium chloride can at this stage be removed to a considerable extent by cooling and crystallizing; and as some of the samples examined contained up to 20 per cent. of the total ammonia going to the stills as ammonium chloride, the recovery of the ammonium chloride as such should yield considerable profit.

The remaining mother-liquor will now contain chiefly thiosulphate, chloride, and thiocyanate. This liquor is placed in a still and neutralized with weak sulphuric acid so as to decompose the thiosulphate. After agitation, such a quantity or more of sulphuric acid of about 120° Tw. is added as would form ammonium hydrogen sulphate with the ammonia contained as thiocyanate. On heating to about 100 C. or less and agitating, the thiocyanate becomes partly decomposed, and partly distils over as such. On passing the gases through limestone, a pure solution of calcium thiocyanate is obtained; hydrochloric acid not being liberated if the temperature and other conditions are followed out according to the above. After passing the calcium-carbonate absorber, the gases are taken through a mixture of an iron salt with alkali, or through oxide-of-iron purifiers; and in either case sulphuretted hydrogen and cyanogen compounds other than thiocyanate are thus removed.

The liquor from this still, which contains ammonium sulphate, chloride, and free sulphuric acid, but no thiocyanate, may be used for diluting the sulphuric acid which is employed in the saturator. It will, however, in existing installations probably be better to use a separate saturating-box built of stone for this liquor, and take part of the ammonia from the main into it, so as to avoid any chance of the lead in the old saturator being attacked by any hydrochloric acid which may be set free. In new installations, the ordinary saturator would serve the purpose if made of material which will resist hydrochloric acid, always provided that it was found that the liquor coming from the sulphocyanogen still attacked lead.

One great advantage of the method is that it enables us to recover the ferrocyanide as well as the thiocyanate without interfering with the plant as it is in use at present. It is well known that many processes have been designed to remove the cyanides and ferrocyanides from the gaseous products of coal distillation by passing them through alkaline emulsions of ferrous oxide. All these processes require special washing apparatus; and in the case of gases from coke-ovens, it is said that the results obtained have been unsatisfactory. Two ways of recovering cyanides and ferrocyanides are open in Grossmann's method. Where the quantity of these compounds is large, they may be removed as insoluble ferrocyanides or zinc ferrocyanides

by adding ferrous or zinc sulphate in exact proportion (to be previously ascertained by test) to the evaporated liquor, and neutralizing carefully with sulphuric acid. After filtering, the liquor may go to the still and be treated with a further quantity of sulphuric acid in order to eliminate the sulphocyanogen. But where the quantity of ferrocyanide is not excessive, there is no need of any treatment of this kind, as the ferrocyanides will become decomposed in the still in presence of an excess of sulphuric acid, evolving hydrocyanic acid, which will be absorbed in the alkaline iron or in the oxide purifier, and thus allow of the recovery of these compounds in the shape of ferrocyanide.

Grossmann contends that the cost of his process should in no case exceed in cost of working that of the present method. There is a saving in not using lime, which amounts to 3s. per ton of ammonium sulphate, and a saving in the quantity of steam used; and the amount of labour should be the same as before. There should be a gain in the yield of ammonium sulphate equal to about 4s. per ton, as no ammonia left in the waste liquors from the stills is eliminated from the system. There is a gain through the recovery of thiocyanate and ferrocyanide, which, taking them at only 1d. per pound, would amount to from 4s. to 20s. and more per ton of ammonium sulphate; and the extra profit on ammonium chloride may be put down at from 9s. to 13s. and more. Against this probable saving of from 20s. to 40s., we have to allow for the cost of evaporation, the cooling of the liquors, and the amortization and depreciation of the extra plant required. The cost of the first item will greatly depend upon local circumstances. Where the amount of water in coal is normal, there should be sufficient waste heat in coke-oven works to render this operation free from being a charge on the process. In gas-works, where there is no waste heat, the charge should not amount to more than 5s. per ton of sulphate of ammonia, as there is always in these works sufficient breeze to spare, which has only a low commercial value, and in some cases almost none. Even where the amount of liquors produced is excessive, it will, in many cases, be found that there will be sufficient waste coal and coke of unmarketable quality which can be used for evaporating purposes. The cooling of the liquor also depends on local circumstances; but, even under the most unfavourable conditions, the charge for it would be small.

The depreciation of the plant could only take place in the evaporating apparatus, which is not expensive. The process has not been designed with a view to effecting a saving in manufacture, but in order to improve it in a sanitary respect. If it will accomplish that without extra charge to the manufacturer, it will have done all that can be reasonably expected.

A new process for obtaining ferrocyanide, by the same inventor, will be mentioned *infra*, Chapter XV.

Treatment of Ammoniacal Liquor in the Cold State for removing Hydrogen Sulphide and Carbon Dioxide.

We have already mentioned, *supra*, pp. 1003 *et seq.*, some of the processes belonging to this class in connection with the manufacture of pure liquor ammoniæ. Here we speak of processes connected with the manufacture of sulphate.

These processes are not much practised. Some have proposed *ferric hydrate*, which acts as follows:

$$Fe_2(OH)_6 + 3(NH_4)_2S = 2FeS + S + 6NH_3 + 6H_2O.$$

Thus ferrous sulphide, sulphur, and free ammonia are produced; the two former remain behind. The residue can be revivified till it is rich enough in sulphur to be utilized for vitriol-making, or for the sulphur to be recovered by distillation. For the latter purpose Gerlach (Ger. P. 229) employs superheated steam, as offering great advantages.

Sometimes *soluble salts of iron or manganese* are added to the gas-liquor before distillation, in order to remove the sulphide. The precipitate might be filter-pressed, and the residue revivified as just mentioned. But this process, like the former, is not very simple and cheap.

A special process for removing sulphuretted hydrogen from gas-liquor is that of Kunheim & Co. (Ger. P. 26422), which aims at fully utilizing the sulphur. The crude gas-liquor is treated in the *cold* state with a strong current of atmospheric air, divided into many jets. This dissociates the ammonium sulphide into ammonia and hydrogen sulphide, the latter being carried away by the air. The gaseous mixture is conducted through finely divided ferric hydroxide, and the hydrogen sulphide is here absorbed. For this purpose native hydrated oxide of iron, or an artificial precipitate, or even other hydrated

metallic oxides may be employed. The ferric hydroxide is kept suspended in a dilute solution of alkaline earths. Fig. 287 illustrates the process. The gas-liquor is introduced by means of a force-pump through the pipe *p* into the boiler K, into which a strong current of air is forced by means of a blast or injector through *l*. The gas-liquor mechanically carried away is retained in the safety-vessel U, and is continually returned into K. The mixture of air, hydrogen sulphide, and a little ammonia is conducted by a perforated pipe into the vessel A, half-filled with a mixture of ferric hydrate and lime-water.

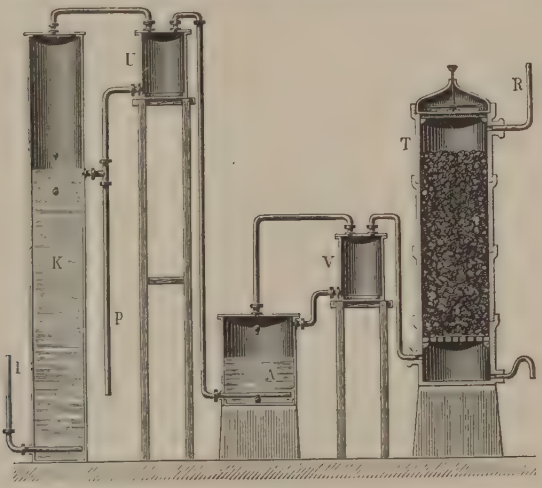


FIG. 287.

Here the H_2S is absorbed, but the FeS formed is at once changed by the air into free sulphur and regenerated ferric hydrate. The excess of air and some ammonia first pass through the safety-vessel V, where so much of the pasty mixture as has been mechanically carried away is retained and flows back into A. From here the gases pass through the stoneware coke-scrubber T, where the ammonia is absorbed by a shower of sulphuric acid. The air escapes through R into the atmosphere, or first into a chimney. The gas-liquor remaining in K, and now freed from sulphide, is in the usual way caustified by lime and distilled. The here-described process of absorbing hydrogen

sulphide by a mixture of ferric hydroxide with lime, with a simultaneous introduction of air for reconverting the ferrous sulphide formed into free sulphur and ferric hydroxide, may also be employed for dealing with hydrogen sulphide from any other source. [It is only right to state that the absorption of sulphuretted hydrogen by a mixture of ferric or manganic hydroxide and lime, suspended in water, was described by myself as early as 1866, in the B. P. 1108; and Weldon, in his patent of 18th August 1871, and again in 1876, added to this the regeneration by air in the liquid state. The simultaneous passage of air, along with the H_2S, through the mixture of ferric hydroxide of lime was also tried by myself about that time, but nothing was published concerning it, as the experiments could not be followed out to a definite issue. *Cf.* also the *Alkali Inspectors' Reports* quoted on p. 1096.]

A somewhat similar process is that of Holgate, of the Halifax gas-works. He submits the raw liquor to a moderate heat, produced by passing the waste gases from the sulphate of ammonia saturator into a box through which the gas-liquor is made to flow in a coil of 2-inch tubes. By this means most of the H_2S and CO_2 is driven off, whilst most of the NH_3 remains behind. A table given on p. 31 of the *Thirty-sixth Report of the Alkali Inspectors* shows that by this treatment only from 16·9 to 26·5 per cent. of the NH_3 is driven out, whilst 54·5 per cent. of the CO_2, and 84·6 per cent. of the H_2S is removed.

Wolfrum (Ger. P. 40215) produces a solution of basic ferric salts by suspending 1 part spent oxide of iron in 2 or 3 parts water, adding ½ to 1 part sulphuric acid or 1 or 2 parts hydrochloric acid, and dissolving in each 50 parts of this mixture 5 or 6 parts iron-ochre. This solution serves for disulphurizing 50 or 60 times its volume of raw gas-liquor. The precipitate produced contains about 30 per cent. sulphur soluble in carbon disulphide.

Fousset (Fr. P. 382269, of 1906; B. P. 25311, of 1907) also employs for the working-up of ammoniacal liquors an apparatus working in the cold. The liquor, after adding fixed alkali, if necessary, is "atomized," and in this condition allowed to fall down a vertical drum, in which it meets an ascending current of air which carries the ammonia with it as gas. This air passes between zigzag partitions, on which it deposits any

spray, and then impinges against a rotating fan which is kept supplied with dilute sulphuric acid.

Kestner (B. P. 1843, of 1906) proceeds in the same way. He atomizes the liquor by means of a Kestner centrifugal atomizer in a current of air, say, 180 volumes of air to 1 volume of ammonia liquor containing 2 g. NH_3 per litre. It will be found that the liquor issuing from the apparatus does not contain more than 0·015 g. NH_3 per litre, so that 99·25 per cent. of the ammonia passes away with the air. In the case of 300 volumes air to 1 of liquor, only about 0·005 g. NH_3 remains after atomization. The air is then passed over sulphuric acid, which takes out all the NH_3, so that this process is practically a cold process for the recovery of NH_3 from ammonia liquors.

Similar processes have been patented by Feld (Ger. P. 188636) and Brandenburg (Ger. P. 189830), and by the Société J. Jean & Cie (Fr. P. 372171).

Warth (*Chem. News*, vol. xciii., p. 259) by agitating gas-liquor with gypsum recovers 80 per cent. of the ammonia in the state of sulphate, so that only one-fifth of the ammonia need be got by boiling and absorbing in sulphuric acid.

Apparatus specially intended for Working Sewage.[1]

A considerable number of these are described by C. Vincent in the *Encyclopédie Chimique*, 2nd section, tome x., part 4, pp. 14 *et seq.*; but most of them present nothing calling for special recommendation, as the older apparatus of Figuera, of Margueritte and Sourdeval, and others; or else they are only various forms of combinations of boilers with dephlegmating-columns and heat-economizers, not different in principle from those already described, as the apparatus of Lair, of Sintier, and Muhé, etc. That of Hennebutte and Vauréal has a very peculiar form, but the principle is still the same. We would refer for descriptions and diagrams of these apparatus to M. Vincent's book; also for that of Chevalet's apparatus for treating turbid sewage and "tout venant," that is, the whole contents of the sewers, including night-soil and all other solid refuse. We will, however, describe two other apparatus constructed for the same purpose.

[1] *Cf.* pp. 844 *et seq.*

P. Mallet's Apparatus for treating Thick Sewage

is shown in Fig. 288. It consists of a tubular heater, A; a tubular vapour "analyzer," B; a cast-iron column, C, 4 feet 8 inches wide, serving as dephlegmator. This column, by means of a hollow stand, rests on the top of the agitating-column E. The latter has a diameter of 6 feet 8 inches, and contains a number of plates with central holes; a central shaft, made to revolve with toothed gear, carries a set of stirrers ranging over every one of these plates. The sludge-decanter F forms the bottom of the whole system. The sludge itself is discharged into trucks, W, whilst the clear, decanted, boiling part of the spent liquor passes on to the heater A, and afterwards, being completely cooled down, runs off through the tube *s*.

The fresh sewage matter is forced by means of a pump through the pipe *a* into the heater A, and passes through its tubes; on its way it gets heated by the spent liquor, circulating in the opposite direction, before issuing at *s*. The sewage then ascends through the 4-inch pipe *b* into the analyzer B, in which it is further heated by the vapours ascending from the rectifier C; it then passes out by the siphon-tube *c* into the column C at its tenth chamber, and descends in this, in order to pass through the tube *d* into the agitating-column E. During this transit the volatile ammonium salts contained in the sewage are carried off by the hot vapours coming from E, and escape through L; the vapours pass through the rectifier C, where they become richer in ammonia, then through the analyzer B, where they give up the remaining water, and at last escape through T into the sulphuric-acid saturator. The uncondensable gases are carried under a fire-grate, to be burned. Before the sewage, deprived of volatile ammonium salts, enters through *d* into E, it is mixed with milk-of-lime pumped in through K, in the proportion of 8 kg. lime to each ton of sewage. The action of the agitating-column E is just the same as that described on p. 1047. The spent matter now descends through the siphon-tube *m* into the sludge-decanter F, 6 feet 8 inches wide, where it suffers an enormous loss of velocity, which, along with the action of the lime on the albuminous substances, promotes a rapid settling of the solid impurities. By means of the two valves at the bottom, the sludge is discharged into the trucks W, and can be filter-

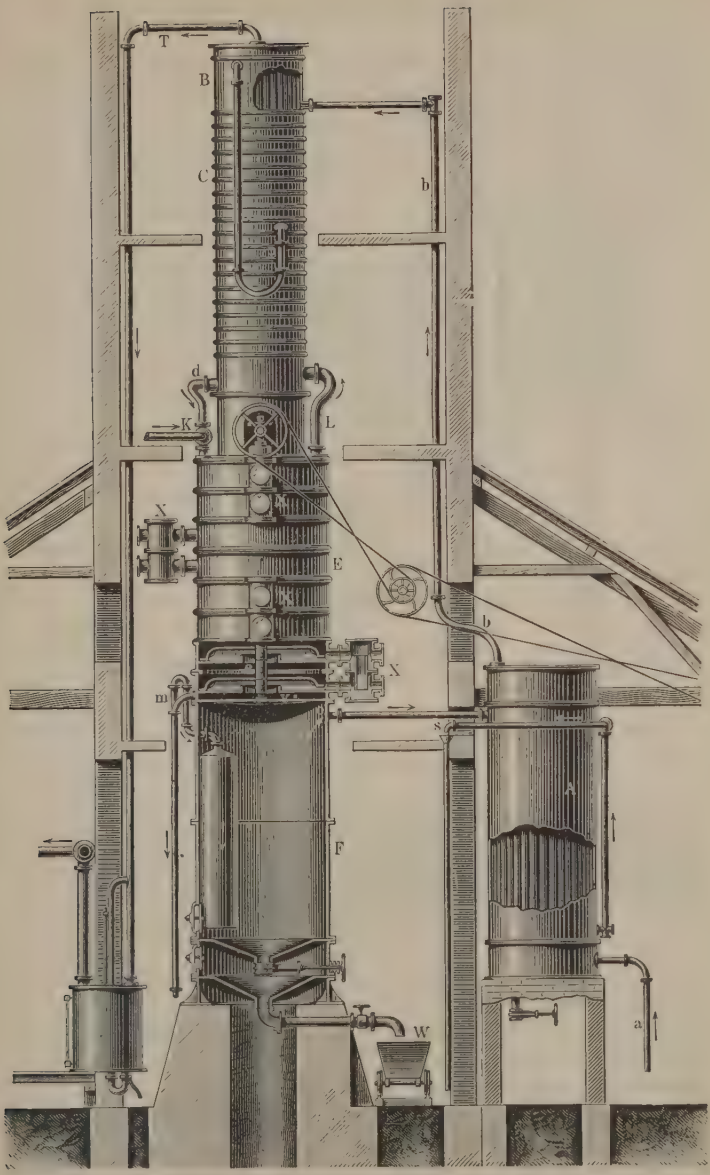


FIG. 288.

pressed before being sent away. The clear liquid issuing from F is used for heating up the fresh sewage in A, as before described. The necessary heat is supplied to this apparatus by direct (wet) steam, through a 1¼-inch steam-pipe, *v*, just above the bottom of E.

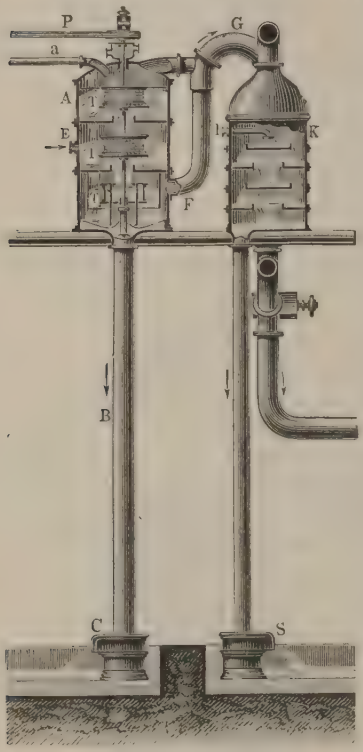


FIG. 289.

This apparatus is capable of treating 65 tons of sewage per 24 hours. It is easy to clean, as all the overflow-pipes are arranged in outside annexes, X X, which are accessible by removing the flanges.

One of these apparatus has been in use since 1881 at La Tresne, near Bordeaux, and several others seem to be working satisfactorily in France.

Lencauchez's Apparatus

works under diminished pressure, and consists of two quite distinct parts. The one shown in Figs. 289 and 290 is called the "barometric chamber," and serves for expelling the volatile ammonium salts. It is a wrought-iron cylinder, A, 7 feet 4 inches diameter and 11 feet 4 inches high, fixed on the top of an iron column, B, of a height of 33 feet, at the bottom of which a siphon-pipe carries off the spent liquor into the tank C. In this "barometric chamber" a good vacuum can be kept up by an air-pump, which continually aspirates the gases and vapours given off by the sewage; this gaseous mixture is, as usual, absorbed in sulphuric acid, whilst the spent liquor runs off at the bottom of the column B, in which the liquid rises equal to the atmospheric pressure. The chamber A is divided

into three compartments, in which as many small turbines, T T T, set in motion by the pulley P, convert the sewage which arrives in the pipe *a*, three times over, into a fine spray, which greatly facilitates the escape of the volatile ammonium salts. The liquor is heated by means of the exhaust-steam of

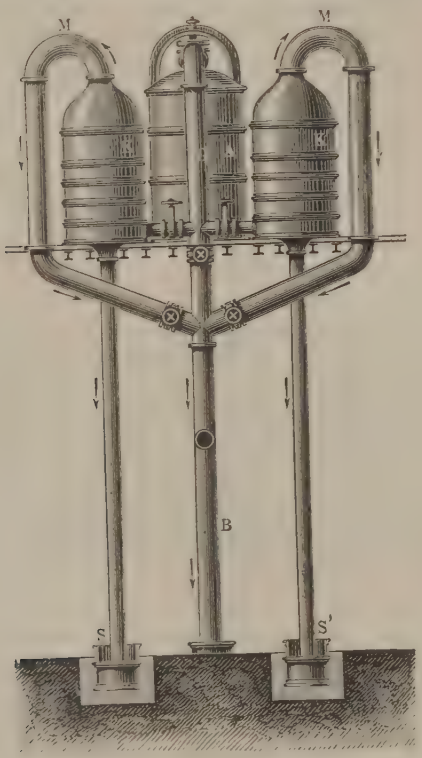


FIG. 290.

the engine, through the pipe E. The steam and vapours, issuing through F and G, pass alternately through one of two saturators, K K', arranged on a principle similar to the chamber A. These are 6 feet wide, and are provided with horizontal diaphragms for dividing the acid into a spray. The quantity of acid and the time it stays in the saturator must be so regulated that all the ammonia is absorbed and yet

the acid is saturated. The solution of ammonium sulphate runs down the column and through the siphon S, into a crystallizing-vessel. The pipes M and M′ carry off the noxious gases, which are aspirated by the air-pumps, freed from moisture by cooling down, and burned in the usual manner. The condensed liquid, which contains a little ammonium salt, is sent into the apparatus to be described next.

Fig. 291 shows that part of Lencauchez's apparatus which deals with the "fixed" ammonium salts. It is a horizontal cylinder, 10 feet in diameter and 33 feet long, provided with a longitudinal shaft and agitating-paddles for mixing the liquor

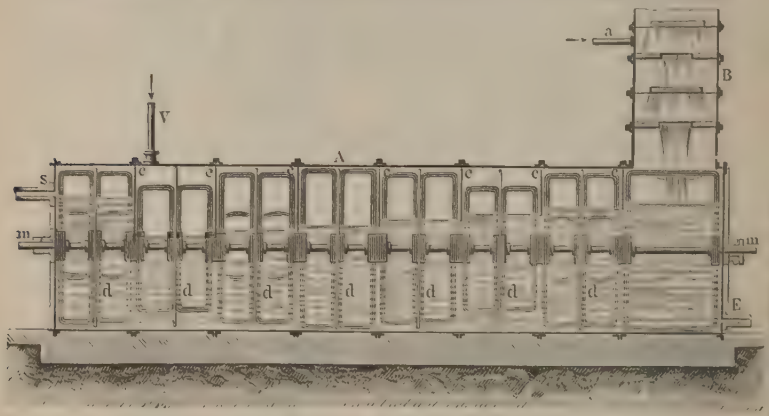


Fig. 291.

with milk-of-lime. Between the paddles there are seven disks for diminishing the speed of transit of the vapours. These seven partitions, *c c c*, divide the cylinder into eight chambers of equal size. The first partition from the left reaches down to the centre of the cylinder; the following ones are each 6 inches smaller than those preceding. A tube, V, enters the second chamber and injects into it the exhaust-steam from one or several steam-engines; the last chamber is surmounted by a cast-iron rectifying-column, B. The first plates of this column have simple holes, without covering-cups, so as not to be stopped up by solid matter projected from below; its upper portion is connected with two reflux-worms and a receiver for crude concentrated ammoniacal liquor. For making sulphate

the worms are not cooled so much, and the vapours from them are conveyed into a sulphuric-acid saturator.

Into this apparatus the liquor, deprived in the "barometric chamber" of its volatile ammonium salts, is introduced through *a*, at the third chamber of the column B; it descends in thin jets, and gets into the horizontal cylinder, where it is mixed with milk-of-lime. The ammonia of the fixed salts is thus set free, and comes off gradually in the different chambers; it passes on successively from one to the other by bubbling through a mixture of liquor and lime, each time traversing a layer 6 inches deep. At last, after about half an hour, the liquor arrives totally spent at the other side of the cylinder, and runs to waste by the siphon-tube S.

This apparatus is very ingeniously constructed, but seems too complicated, and has not made its way outside of France. It is doubtful whether the very much simpler means employed in England and Germany do not answer the same purpose quite as well.

Mylius (Ger. P. 66465) proceeds without distillation, by means of a vacuum. The sewage, clarified by lime, runs down upon cloths suspended in an evacuated chamber, where also sulphuric acid runs down asbestos-cloth and absorbs the NH_3. Seiffert (Ger. P. 71414) also employs a vacuum, in a column containing a number of dishes filled with sulphuric acid, on a similar principle to the last.

All processes for obtaining ammonia from sewage at the present time have hardly more than a sanitary interest, the great bulk of ammonia being supplied by the distillation of coal.

Arrangements for absorbing the Vapours in Sulphuric Acid (Saturators); Finishing the Sulphate.

The apparatus intended for this purpose, called the *saturator*, must be so constructed that, on the one, no ammonia escapes absorption in the acid, and, on the other, the gases set free (carbon dioxide and sulphuretted hydrogen) do not become injurious to the workmen and the neighbourhood. In explaining a number of special apparatus we shall meet with various constructions of saturators; here we only mention the general principles to be observed.

In one kind of saturator the gas, partly or mostly dehydrated by dephlegmation, is condensed in *dilute* sulphuric acid, so that no salt is separated during the saturation. The solution formed is clarified by repose, and is then evaporated, mostly in lead pans by means of a steam coil, up to crystallization, during which operation an offensive smell is given off. The mother-liquor is employed for diluting a fresh quantity of sulphuric acid. In another kind of saturator the ammoniacal vapours are absorbed in somewhat *concentrated* sulphuric acid (say, 140 Tw.), in which case the ammonium sulphate separates in the solid state in the saturating-vessels, and is fished out of them from time to time. More acid is run in continuously in a thin jet, so that the saturator is always kept filled up to about the same level. The second process has the advantage of being continuous and saving all evaporation, but possesses the drawback that the liquor cannot clarify, and the salt does not come out so pure as in the first process.

The saturators differ in form as follows:—That intended for dilute acid is a closed tank lined with lead, partially filled with sulphuric acid at 80 to 100° Tw.; the ammoniacal vapours arrive in a pipe, which branches out at the bottom of the tank, and is there provided with many holes for the issue of the ammoniacal vapours. The gases liberated by the decomposition, along with a large quantity of steam generated by the heat of the reaction, are conducted away by a pipe from the upper part of the vessel, and are disposed of in various ways, to be described hereafter. The passage of vapours into the vessel is continued until a sample, drawn from a tap, shows that the acid is sufficiently saturated. It is best to leave a slight excess of acid, in which case the liquor, after evaporation in leaden pans by indirect steam, yields whiter sulphate.

With more concentrated acid another form of saturator is used consisting of a tank not completely closed, to which, as the acid becomes saturated, more strong acid is added, either from time to time or in a continuous thin jet. The waste gases and steam in this case are drawn away from the closed part of the tank by means of a chimney-draught, which must be strong enough not to allow any gas to escape out of the open portion; this can be still better secured by a fan-blast or an injector. As the solution becomes supersaturated with ammonium sulphate,

this salt crystallizes out, in spite of the heat. In some cases this is continued till the liquor becomes too thick, whereupon the whole contents of the saturator are drawn out by means of a bottom tap into a cooler, from which, after the crystallization is complete, the mother-liquor is pumped or ladled back again into the saturator. In other cases the salt is fished out of the saturator during the operation itself. This is done in a "fishing-box," represented in Fig. 292. It consists of a wooden vessel lined with lead, and divided into two compartments by the lead curtain *a*, which dips into the acid. The outer compartment is lower and open at the top; the bottom is made to slope to this side. The other compartment is closed by a lid, perforated for the tube *b*, through which the ammoniacal vapours arrive, for the exit-pipe *c*, and the acid-pipe *d*. The sulphate precipitating during the operation is raked towards the open end, and fished out there from time to time by a perforated ladle. The best form is that in which the bottom of the open compartment is made into a well, in which fits a strainer; the salt drawn from the closed compartment falls into this strainer, which from time to time is lifted out to empty the salt. Fig. 293 shows this arrangement.

A saturator constructed on this principle, which has long been well known to practical men, and has been in use at many works (it is also described and figured in my German work of 1867), has been patented by W. Arrol and J. Meikle (B. P. 12174, of 1884). The only novelty their patent contains is that their vessels are not made of lead, but of copper—an invention not likely to be infringed by others.

Watson Smith (priv. comm.) recommends the following plan for obtaining perfectly white sulphate:—The saturator is charged with acid at 80° Tw., and ammonia is passed in until there is a slight smell of it. The excess is neutralized by a little acid; and the separated sulphate is *at once* fished out, whereupon the operation is commenced again. If, however, the acid is run in little by little, and the gas passed through for a long time, the separating sulphate is black; and so it is in the former case, if, when the liquor has been proved by its smell to contain an excess of ammonia, fresh acid is run in and fresh gas is passed through, without fishing out the sulphate already formed, so that it is allowed to accumulate.

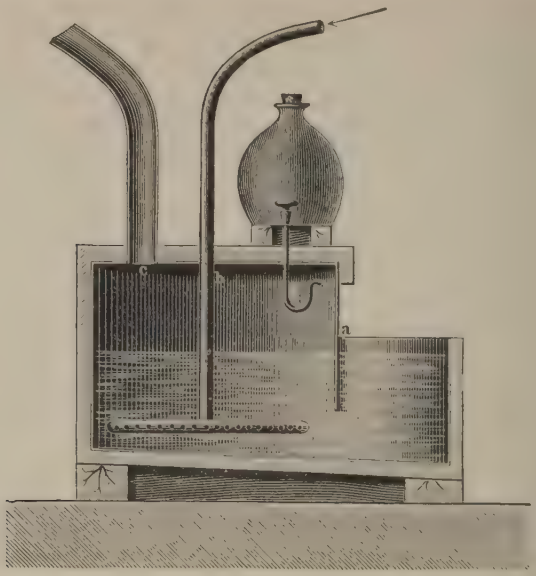


FIG. 292.

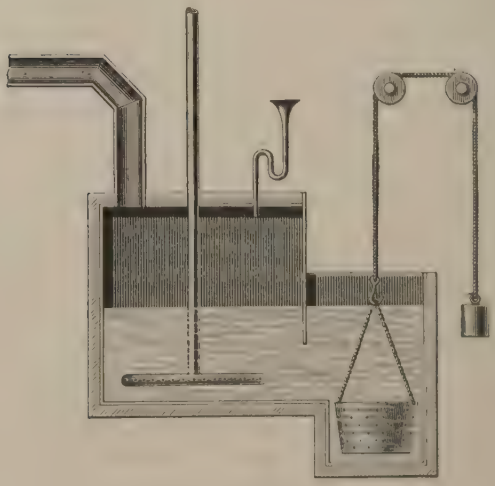


FIG. 293.

In fact the rule is, to fish out the *freshly deposited* sulphate from *tolerably acid* mother-liquors. The fishing is done by means of a ladle of galvanized iron, perforated with numerous small holes; the sulphate is thrown upon a lead-lined drainer, from which the mother-liquor runs back into the saturators.

In the case of discontinuous saturators, it should not be forgotten that solutions of ammonium salts, when boiled, give off some free ammonia. Hence the acid, when nearly saturated with ammonia, hot as it is, will not completely retain it, especially if the bubbles of gas are rather large. For this reason the points of contact should be multiplied, and the gas-pipe should not dip too low into the acid. In the case of very large apparatus, it might be best to employ two saturating-boxes in succession, the upper one to be charged with fresh

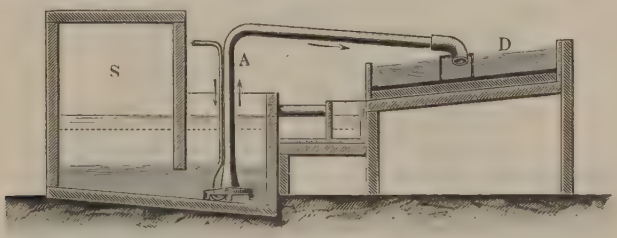


FIG. 294.

acid; the gas would have to pass first through the lower box, where it would give up nearly all its ammonia, the rest being absorbed in the upper box. When the contents of the lower box have been run off, those of the upper box should be run down into it, and fresh acid charged into the upper saturator.

The reaction between the ammonia and the sulphuric acid produces so much heat that the liquid soon reaches nearly its boiling temperature. This, in the first instance, produces a very welcome, constant agitation; secondly, it prevents the condensation of steam and keeps the liquid at higher concentration.

Wilton's apparatus (Ger. P. 54827; *Gas World*, 1890, p. 717) is shown in Fig. 294. The sulphate formed in the saturator S is continuously lifted by the injector A on to the draining-plate D, from which the mother-liquor runs back into the saturator. This arrangement saves much labour. Four saturators can be supplied by one ejector, which throws out 26 tons of sulphate

per day, and the regular removal of the salt admits of raising the production of the stills by 20 per cent.

Sauer (Ger. P. 70185) (Figs. 295 and 296) passes the ammonia through a_1 b into the saturator c, the H_2S escaping from the bell d through pipe d_1 into the dust-collector d_2, and thence into the chimney or into a purifier. The sulphate is not fished out, but acid is generally run from box c through funnel e into the bell, until all is saturated. The ammonia is now passed into another saturator, tap a_2 is closed, and the salt fished out of the first saturator.

Kennedy (B. P. 1653, of 1890) describes some improvements in ordinary saturators with slanting bottoms.

Colson's saturator (*Alkali Inspectors' Report*, No. 32, p. 63)

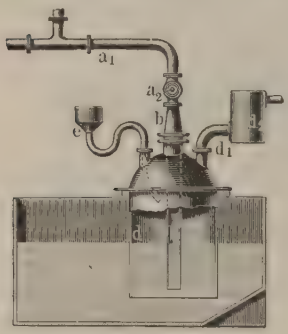


FIG. 295.

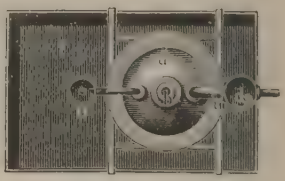


FIG. 296.

has a conical bottom of the proper shape, as shown here (Fig. 297), and a simple outlet valve, consisting of a copper disk pressed against the mouth of the outlet-pipe by means of a screw. The vessel is made of cast-iron with lead lining. The valve is fixed in such a position that the salt is removed as soon as it forms, as shown by the inspection-pipe in the middle of the saturator.

Ellery's saturator (*Gas World*, 1895, p. 783) (Fig. 298) is very similar to the above, but is made of wood lined with lead, with a simple trap-valve at the bottom. The acid is heated up before entering the saturator by the hot waste gases.

Carulla (*J. Soc. Chem. Ind.*, 1903, p. 607) points out that the saturator should be provided with safety-valves, the absence of which once caused an accident at his works.

Duggan (B. P. 5011, of 1896) describes again the well-known arrangement, according to which the upper part of the separator is cylindrical, while the lower part is conical or curved, to promote the discharging of the sulphate.

Ballantyne (*J. Soc. Chem. Ind.*, 1903, p. 794) keeps the whole

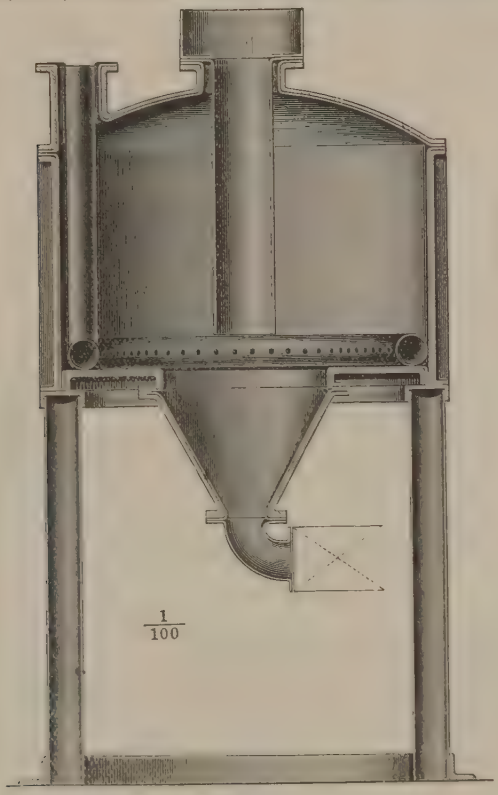


FIG. 297.

apparatus under a vacuum. All overhead tanks can thus be dispensed with, as the liquor and the acid can be drawn into the still and saturator from any place a little above the floor level. He finds that the best time for "salting out" is when the liquid in the saturator is at 56° to 57° Tw. The vacuum on the pump and saturator should be 23 to 24 in., and that on the still 13 to

15 in. of mercury. The total consumption of fuel is 4 cwt. of coke per ton of ammonium sulphate. For the saturator he uses a special discharger (B. P. 27070, of 1902), which at its neck has a seating against which an upwardly closing cone, attached to a vertical spindle passing through a stuffing-box in the bottom, can be screwed up by mechanical means. When the discharger is full of crystals, the valve is closed, and a sliding door is moved upwards to admit of removal of the contents of the vessel.

Schwab (B. P. 17585, of 1903) avoids the drawbacks attached to cast lead or iron saturators by employing a saturator with body and top made in one piece of lead, with a fender attached

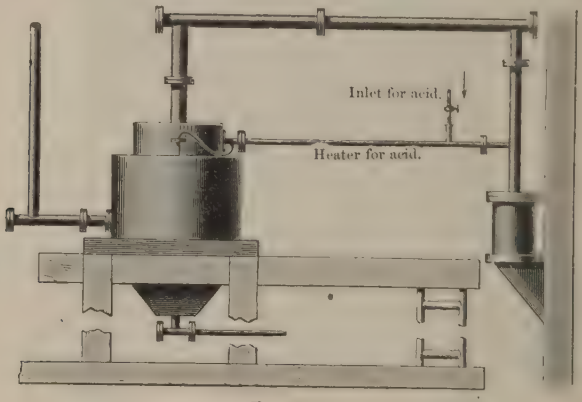


FIG. 298.

to the body, a bottom extending under the body and fender, and an aperture formed at the base of the body, making a passage between this and the fender. This and the body may be formed out of one sheet.

Heuss (priv. comm.), instead of lead or lead-covered iron, employs saturators made of earthenware, capable of resisting both acids and changes of temperature.

Rosenkranz (*J. Gasbeleucht.*, 1904, p. 459; *J. Soc. Chem. Ind.*, 1904, p. 602) employs two saturators in rotation, so that the acid in one of these can be completely saturated in the first, and the remaining NH_3 completely absorbed in the second, whereupon the gaseous current is reversed, so that the second saturator now comes first.

Zimpell (Ger. Ps. 161718 and 170807; Eng. Ps. 6891 and 23379, of 1904; U.S. P. 782637) recovers the ammonia not

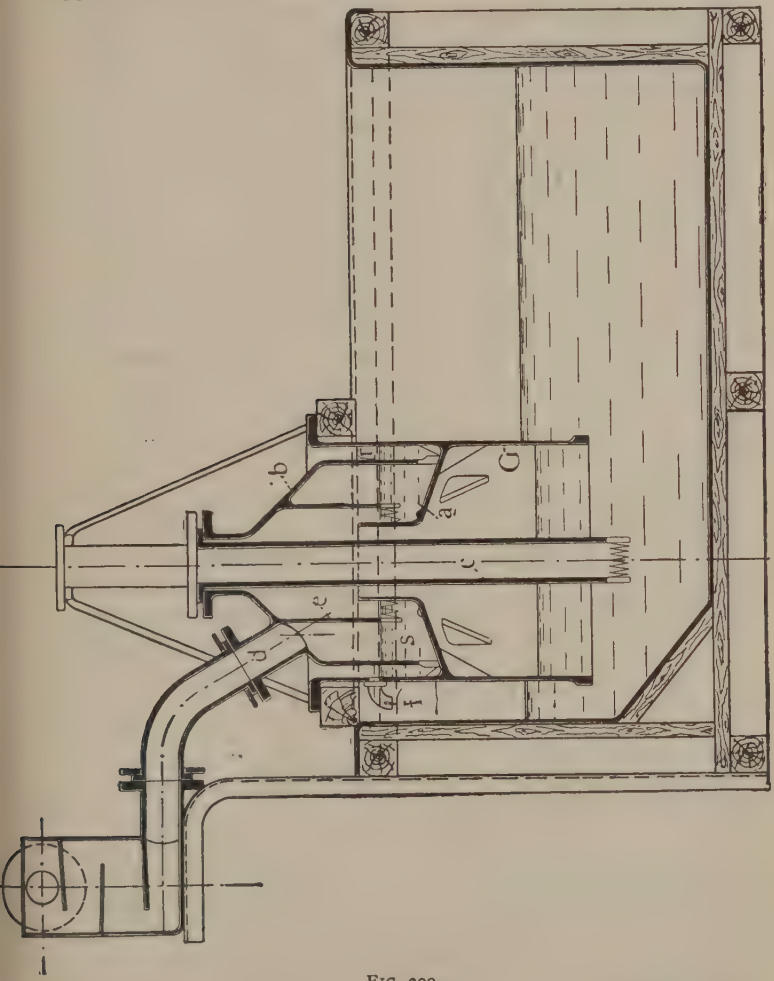


FIG. 299.

absorbed the first time by a second saturator combined with the first, on the following principle. When dry vapours of water and NH_3 are passed through the first saturator, no water is

condensed in the liquid form, since the heat produced by the combination of the NH_3 and the acid keeps the steam at a sufficiently high temperature. In the second saturator, however, where but little heat is generated, there is a constant condensation of water and consequent dilution of the acid. To prevent this, the inventor combines both saturators to one apparatus, as shown in Fig. 299. It is a combination of two bells, in such a way that the crown *a* of the lower bell G forms the floor of the upper bell *b*. Above this floor there is a scolloped wall *e*, which acts like the dipping tube in an ordinary saturator. The gases issuing through pipe *c* from the lower, principal saturator, before being carried away through *d*, play round the upper saturator and keep it at such a temperature that no steam is condensed to liquid water. This apparatus is built by the Berlin - Anhaltische Maschinenbau - Aktien - Gesellschaft ("Bamag").

The following data give comparative results with an ordinary saturator and bell and with the new double bell. The liquor used in both was the same, 1·18 to 1·19 per cent., and was fed in equally; the acid was a mixture of saturated acid with fresh acid of 58° Baumé. The ammonia in the waste gases was determined by cooling them to 26° C. and finding the amount of ammonia in the condensates. With the old apparatus, the loss went on rapidly increasing from hour to hour; with the new, it remained very uniform for some hours and then fell off. In more detail, we have—

	Old Apparatus.	New Apparatus.
Liquor treated, cubic metres . . .	8·150	10·100
NH_3 therein, kilograms	96·985	119·180
NH_3 run off in the liquor, kilograms . .	0·235	0·292
NH_3 led into sulphate plant, kilograms .	96·750	118·888
Loss in the saturator, kilograms . . .	6·307	0·773
Loss, percentage of NH_3 led in . . .	6·575 "	0·650
Duration of experiment, hours . .	9½	12
Loss of NH_3 in third hour, kilograms . .	0·089	0·082
" " sixth " "	0·388	0·095
" " ninth " "	1·554	0·102
" " twelfth " "	—	0·015

The contents of the supplementary saturator were kept at sp. gr. 1·45 to 1·52 by addition of acid, the excess overflowing into the saturator proper; this was emptied out every 6 or 7 hours. The sulphate from the new apparatus was brighter than that from intermittent saturation, and it contained less arsenic and iron, which were easily removed with the froth on the acid in the supplementary saturator. The acid removed from the saturator proper and separated from sulphate by draining or centrifugation could be used over again, not having been diluted. This apparatus is also made by the Berlin-Anhalt. Masch.-Akt.-Ges. ("Bamag").

A new acid-saturator, constructed by the Berlin-Anhalt. Masch.-Akt.-Ges. (Ger. P. 165308) provides a plate with nicked margin, which can be raised or lowered for closing the inner bell. During the work this plate is lowered, and forms a gas-lute, but it is raised when fresh acid is run in.

Clarke, Chapman & Co. and Robson (B. P. 27840 A, of 1905) employ for the absorbing acid, a closed tank divided by partitions which must be passed by the gases in a zigzag way.

Langlands & O'Connor (B. P. 17267, of 1905) construct the absorbing vessel of porcelain or enamelled stoneware, using lead only for connecting pieces.

Williams & Fenner (B. P. 25547, of 1906) fix a distributing pipe for steam and ammonia externally to the saturator, communicating with it by means of a number of symmetrically placed short connecting pipes. In this way the sulphate is formed equally throughout all parts of the acid liquor, and incrustations are avoided.

A saturator constructed by Hartmann is described by Peters in *J. Gasbeleucht.*, 1906, p. 164.

Thiel (Ger. P. 193218) employs an apparatus consisting of two bell saturators. The gases first pass through the upper one, and from the top of its bell they pass on to the lower saturator, where they have once more to pass through sulphuric acid. This lower saturator has a double leaden bell. Openings are provided which ensure a good circulation below and outside the lead bells, without allowing the gases to escape below their bottom. The inner bell is at a temperature above the boiling point of water, the outer one is much colder. This produces a circulation of the liquid in this saturator.

The saturator of Plzak (Ger. P. 189473) is divided by partitions, and the compartments thus formed are charged with acids of different concentration. The gases are first passed through weaker acid, which absorbs most of the ammonia, and then through strong acid. After some time some acid is run from the latter into the former compartments, and is replaced by fresh acid.

Koppers (Ger. P. 181846) prevents dilution of the bath in the saturator by reheating the gases from a still, which had been previously cooled for the purpose of separating the tar, by means of the excess heat of the crude gas or other waste heat.

Brunck (B. P. 8287, of 1903) passes the vapours into concentrated sulphuric acid at a temperature not lower than 80° C.

Feldmann (B. P. 11525, of 1902; Ger. P. 134976) arranges a second saturator over the first, connected with it by an overflow opening into the bell of the lower vessel, which is thus supplied with relatively fresh acid. A similar principle is employed by Koppers (Ger. P. 140350).

Chatfield (Ger. P. 82443) employs technical "nitre cake" (the residue from the manufacture of nitric acid, consisting of an impure sodium hydrosulphate) for the absorption of ammonia.

Pallenberg (B. P. 5657, of 1908) covers the lead coating of the saturator with plates of acid-proof material, bound by means of an acid-proof binding medium. The bell or partition wall of the saturator may be constructed entirely of such material, but in this case the crown or cover of the bell is attached loosely with putty to the cylindrical portion, with an outer cover, bolted on, keeping the whole right, and yet allowing each part to expand individually; cracking of the bell is thus avoided.

Frerichs (U.S. P. 905415, of 1908) combines ammonia with ammonium hydrosulphate and heats the normal ammonium sulphate thus formed so as to give ammonia again, and acid-ammonium sulphate or pyrosulphate to be re-used in the process. If the ammonium sulphate contains nitrogenous and other carbon compounds, it may be purified by heating the impure salt in a blast of air to such a temperature that the volatile carbon compounds are volatilized or oxidized, and the

nitrogenous compounds are converted into ammonium sulphate by reacting with the sulphuric acid of the ammonium salt.

Erlenbach (Ger. P. 203309, Jan. 10, 1908), in order to retain the ammonia coming from the saturator when the acid is nearly saturated, allows these gases to meet the suphuric acid intended to flow into the saturator. This has been done previously, but if, as hitherto usual, the acid is at the strength required for the process within the saturator, the temperature rises too high in the lead-lined apparatus where the gases meet this acid, and the lead lining is rapidly destroyed. This is avoided by employing only a portion, say one-fifth, of the sulphuric acid for the purpose in question; running four-fifths straight into the saturator, diluting the last fifth with rather more than its weight of water, and employing this dilute acid for absorbing the NH_3 escaping from the saturator. The temperature in this case never rises above 109°, and the NH_3 is completely retained.

Quality of the Absorbing-Acid.

A point of some importance is the *quality of the acid employed.* In England, frequently, *sulphuric acid made from brimstone* is used in the manufacture of sulphate of ammonia, because pyrites-acid contains iron and arsenic, both of which discolour the sulphate. F. C. Hills (B. P. 3257, of 1878) avoids this by allowing the pyrites-acid to meet with an excess of ammonia, which precipitates iron and arsenic (?); the excess of ammonia is absorbed in another vessel, in the manner described in the patent. In Germany nothing but pyrites-acid is used; the resulting sulphate has a grey tinge, but is as valuable for manure as the best white. Such grey sulphate is also very commonly found in England. The pyrites-acid ought, however, to be made from pyrites containing very little arsenic; that made from Spanish pyrites (which is now practically the only one used in England, and is often employed in Germany as well) is objectionable because it contains too much arsenic, which produces yellow sulphate—a colour not at all liked by the consumers. Some German makers produce white sulphate, even from strongly arsenical acid, by skimming off the arsenic trisulphide from the top of the saturator, which, of course, necessitates an open form of this apparatus. W. A. Meadows

(B. P. 5520, of 1884) purposely adds a small quantity of tar, pitch, oil, fat, or the like, and carries on the operation at a temperature not below 38° C. In this case a scum is formed on the top, which contains the arsenic and iron of the sulphuric acid, and facilitates their removal. An American patent by E. A. Falls (No. 318972) covers the same invention. A much better process, which the author saw at a Dutch factory, where it had been in use most successfully for a number of years, is the following :— Ordinary pyrites acid is used, of sp. gr. 1·71. To this a certain quantity of "*vitriol-tar*" is added ; that is, the sulphuric acid which has served for washing crude benzol, and which is charged with a large quantity of tarry impurities (p. 685). On the acid being saturated by the ammonia coming over, the tarry matters are precipitated and rise to the surface, carrying along and enveloping the arsenious sulphide formed at the same time from the pyrites-acid. The scum is carefully removed, and the sulphate fished out after this is perfectly white, as I could see from the large quantity kept in stock. Thus the "vitriol-tar," which formerly was an intolerable nuisance, is utilized not merely for its acid, but even its tarry impurities are made to serve a very useful purpose. A similar, but much more complicated, patent process has been previously described.

The prejudice against pyrites-acid seems to be likewise decreasing in England. At least at one of the very largest ammonia-works the author was told that they used it as well as brimstone-acid ; the sulphate made from the former was somewhat discoloured, but fetched exactly the same price as the white sulphate made from brimstone-acid.

Sulphuric acid in the form of a spray is employed for absorbing ammonia by Neumayer and by Wellstein.

Sulphurous acid has been employed for this purpose, with the idea of converting the sulphite into sulphate by the action of air, partially or entirely, by Laming, in 1852 ; by G. E. Davis ;[1] by Addie, for absorbing ammonia direct from blast-furnace gases (p. 909) ; by Young (*cf.* later on) ; by A. M'Dougall (B. P. 15496, of 1884), who passes kiln-gases from sulphur- or pyrites-burners into an ordinary saturator, and

[1] *J. Soc. Chem. Ind.*, 1883, p. 521.

oxidizes the crystallizing ammonium sulphite to sulphate [so far there is nothing new in the patent], while the mother-liquor, containing sulphite as well, is used for scrubbing coal-gas, in which case it absorbs ammonia and decomposes the hydrogen sulphide with precipitation of sulphur; and by Deck (B. P. 17050, of 1887).

Treatment of the Sulphate taken out of the Saturator.

The crystallized mass taken out of the saturator is first put on an inclined wooden bench, preferably covered with sheet lead, and placed in such manner, that the draining off liquid runs back into one of the saturators. Sometimes the sulphate is simply taken away from these drainers after a few hours as it is, and sent out into the market. It is, however, best to drain it more thoroughly by passing it through a centrifugal, and at many works the sulphate after this treatment, when it retains only 2 or 3 per cent. water, is completely dried on plates heated by a coal- or gas-fire. The storeroom for the sulphate should be lined with asphalt or other acid-proof substance.

In Germany the sulphate of ammonia is usually sent out in bulk in closed railway trucks. In Great Britain, however, and everywhere for the export trade, it is packed in bags, holding about 2 cwt. each.

Prevention of Nuisance from Ammonia-works.

Ammonia-works, if not quite properly constructed, may be a great nuisance to the neighbourhood. The sources of this are various, and will be dealt with *seriatim*.

1. *The reception, transportation, and storage of the Ammoniacal Liquor.*

These operations can be made innocuous wherever the sulphate-works are within reasonable distance of the gas-works which produce the ammoniacal liquor, by conveying it by means

of pipes. Dr Ballard recommends underground pipes; but we should decidedly prefer overground pipes, wherever possible, as in the former leakages may occur and continue for a long time without being detected. Wherever the liquor has to be conveyed to a greater distance, tank-waggons or barges are employed, exactly like those used for conveying gas-tar, and similar precautions should be taken in both cases. Pipes should be laid from the gas-works to the place of loading; the tank or hold of the boat should not be covered with loose planks in the perfunctory way often noticeable, but closely; the tar or liquor should be introduced by a close conduit, and, to prevent all nuisance, provision should be made for the escape of air from the tank through a box containing trays charged with hydrated iron peroxide. Tank-waggons should be charged from elevated reservoirs by a hose, through a manhole at the top, without exposure to the air; the manhole is afterwards closed by a tightly screwed-down lid. On arriving at the sulphate-of-ammonia works, the liquor should be run or pumped into the reservoirs with similar precautions, the vent through which the air must escape being guarded by a small oxide-of-iron purifier.

2. *Leakages about the Apparatus.*

These may cause local escapes of foul gases. This may occur about the angles or edges of the curtain in fishing-boxes, by lids not being properly fastened down, by insufficiently luting the curtain with liquor, and the like. Nuisance arising from such cases can be instantaneously detected by those in charge of the works, and may be prevented by ordinary care.

3. *Treatment of the Condensed Water.*

The gases escaping from the saturator, consisting principally of CO_2 and H_2S, carry very much steam along, which must be condensed by cooling before dealing with them by combustion, etc. (see next page). The condensed water is, on account of its extremely objectionable smell, called "devil's water," and is not very easy to deal with. If mixed with the lime-mud, it

renders the latter all the worse to remove. Allowing it to drain away in the soil is not always practicable. Some run it into the ash-pit of the gas-retorts. The best method is to run it back into the stills; but this causes waste of fuel. Where the sulphuretted hydrogen is removed by oxide-of-iron purifiers, the "devil's water" can be filtered through the spent oxide. This can be avoided by taking away the water at the hottest part of the condensing-apparatus, where it contains so little H_2S that it may be run away without any trouble, but then the gases are not very well dried and are more difficult to treat.

4. *Waste Liquor and Lime-mud from the Stills.*

Usually these waste liquors are discharged while hot, and the slight proportion of ammonia they contain is then given off, and causes a very perceptible smell in the neighbourhood. The obvious remedy is, to thoroughly exhaust the liquors.

Lubberger[1] estimates the ammonia in waste still-liquor as follows:—Into a round-bottomed flask, holding 400 c.c., three lumps of quicklime of the size of a walnut are placed, the flask is half-filled with liquor, hot from the still, a cork is inserted, and the whole shaken up, until it takes a dark brown colour. When the lime has been slaked, the flask is cooled under a water-tap, 50 c.c. is filtered into a beaker, and titrated with seminormal hydrochloric acid until the brown colour suddenly changes to light yellow. From the acid employed, the quantity required by the dissolved lime is deducted; the remainder has been used for NH_3.

Dr Ballard mentions that Mr Steuart, of Clayton, reduces the ammonia in the liquor down to 0·002 per cent. The hot waste from the still should not be conveyed away by an open channel, but by a pipe. Before reaching a common sewer or public watercourse, it must necessarily pass through a settling-tank, both in order to separate the solid refuse from the liquor, and to completely cool the latter before it gets into any sewer with which house-drains communicate, or into any watercourse in which fish exist. The settling-tank should be covered over,

[1] *Z. angew. Chem.*, 1899, p. 109.

and should be ventilated merely by a pipe of sufficient length to condense any vapours rising through it. The lime deposit (which contains a great deal of calcium sulphide) should never on any account get into the sewers or watercourses, where it is sure to give off sulphuretted hydrogen. Even when it is entirely kept back in the settling-tank, it may cause nuisance when being disturbed for removal, and again when depositing it on a heap. It should therefore be removed as expeditiously as possible, and with all imaginable precautions against unnecessary exposure to the air. It should be covered up during transmission from the premises, and if shot down in any open place where it is likely to be a nuisance, the surface of the heap should at once be covered with earth and patted down. Wherever that is not possible, it is best to excavate large pits in the ground, which, after being nearly filled with waste lime, are covered up with soil again. But in this case care must be taken that no nuisance arises by foul drainage from such pits.

In some cases such lime-deposit may be utilized by grinding it up with a little fresh lime and a good deal of cinders or the like, when it will form a very well-setting and somewhat hydraulic mortar, which approaches in composition the well-known Scott's cement.

Even when the waste liquors have been completely clarified by repose, and have been practically freed from ammonia, the neighbours or the public authorities often oppose their discharge into public watercourses, on account of the tarry matters, which give them a brown colour and a certain smell. Such opposition is even sometimes founded on quite unreasonable grounds, as the presence of calcium chloride, which, of course, is equally unavoidable and harmless; but the same cannot be said of the tarry matters, etc. Sometimes, owing to the presence of such matters, the liquors will not even readily clarify. In such cases a remedy, as I have convinced myself by experiment, is nearly always possible by producing in the liquor a precipitate of hydrated oxide of alumina or iron, which carries down the tarry matters and other impurities, and leaves a nearly colourless and quite inoffensive liquid. Such a precipitate is caused by adding a sufficient quantity of sulphate of alumina, or, preferably, of sulphate or chloride of iron, along

with sufficient lime to completely precipitate the metallic base, but no more.

König[1] found in waste liquor from ammonia-stills 20·453 g. solid residue per litre, containing :—

Calcium sulphocyanide	2·328
Calcium sulphide	2·563
Calcium thiosulphate	1·091
Calcium sulphate	0·578
Phenols, etc., extracted by ether	0·608
Lime	6·448
Other matters, partly combined with lime	6·805

(Evidently this liquor had not been clarified.) The deleterious effect of such liquor is usually ascribed principally to the sulphocyanide, although this is not quite certain. Where the sulphocyanide is recovered from it (cf. *infra*), probably no nuisance will result from this quarter, except where the spent liquors are submitted to the "bacterial" treatment, since phenols are poisons for the bacteria. P. F. Frankland and H. Silvester (*J. Soc. Chem. Ind.*, 1907, p. 231) found that the average contents of the spent liquors examined by them was 153·8 parts of sulphocyanide (the maximum 171·7 parts) per 100,000, the average contents of the sewage containing such liquors being 9·3 parts in 100,000. Gold-fish can live at least 24 hours in solutions containing up to 250 parts CNS per 100,000; at 450 parts they showed signs of distress; at 500 parts they died. But bacteria are much more sensitive; Bacillus coli communis suffers even at 10 parts CNS in 100,000. The sulphocyanide is not destroyed in the septic tank.

Skirrow (*J. Soc. Chem. Ind.*, 1908, p. 58) estimates the amount of phenols lost in the spent ammonia liquors at 0·37 to 0·55 lb. per ton of coal carbonized, against 0·53 lb. recovered in the tar, so that about half of the phenols produced in the gas-retorts is lost in the spent liquor. He estimates the quantities of substances, contained in these liquors, per 1000 c.c. of effluent, expressed as sodium salts, at :—

Tar acids	2·12 grams.
Sodium thiocyanate	3·14 „
Sodium thiosulphate	1·58 „
Sodium ferrocyanide	0·28 „

[1] *Verunreinigung der Gewasser*, Berlin, 1887, p 354.

G. Fowler (*Forty-fourth Report of the Alkali Inspectors*, p. 51) found that the bacteria oxidize the thiocyanate to sulphate. The spent liquor absorbs 250 grains oxygen per gallon; the effluent afterwards on the average only 22 grains.

Diamond (B. P. 15543, of 1899) clarifies the spent liquor, after settling out the mud in the ordinary way, by means of alumina ferric cake which is afterwards removed by means of a filter-press.

Recovery of Sulphocyanide (*Thiocyanate*) *and Ferrocyanide.*— We have previously (p. 1052) discussed Grossmann's process for working-up ammoniacal liquor without the formation of a noxious effluent and with recovery of sulphocyanides and ferrocyanides. Later on (*J. Soc. Chem. Ind.*, 1908, p. 394; B. P. 7932, of 1907) Grossmann again treats the question of dealing with the effluent, particularly in view of his new process for treating the crude gas-liquor for the extraction of cyanides before distillation (*supra*, p. 1052). The simplest method is to run that effluent into disused pits, but these are available only in special localities, and even there it might find its way into courses used for domestic water. The evaporation of these liquors to dryness is too costly, their use for coal-washing or coke-quenching also leads to trouble. The attempt of using them in steam-boilers has hitherto failed, principally owing to the formation of thick scales of calcium sulphate, but not, as formerly assumed, through a corrosive action of the sulphocyanide upon the iron, which action, as found by Grossmann, is not serious even at a pressure of 40 to 50 lb. per sq. inch. His own process for dealing with the effluent consists in removing the sulphates by means of barium carbonate, according to the reaction:

$$CaSO_4 + BaCO_3 = CaCO_3 + BaSO_4.$$

This reaction does not take place at once, even on shaking for a considerable time, but after settling for 8 or 10 hours the clear liquor is absolutely free from sulphates. For practical reasons one should employ an excess of barium carbonate which is not lost, if the settlings are used for a second operation, adding only as much barium carbonate as had been decomposed. Only after a good many, say twenty, operations the bulk of the precipitate will compel its removal,

and even then there is no loss, since by levigation the barium sulphate can be separated from the calcium carbonate, and its value will pay for the barium carbonate lost.

The agitation with barium carbonate may be performed in a continuous washer; the liquid is passed through settling tanks and after about 12 hours it is clear enough for use in the steam-boilers. Of course the solids dissolved in it will accumulate in the boilers, and after a certain time a certain quantity will have to be blown off every day. These blow-offs, as well as the final blow-off at the time of boiler-cleaning, may be treated for the recovery of thiosulphate or sulphocyanide, or evaporated to dryness in a special furnace, which is now feasible, as its bulk is only one-tenth or even less of the original volume.

Grossmann estimates the cost of this process for eliminating the sulphates from the effluents to $\frac{1}{4}$d. to $\frac{1}{2}$d. per ton of coal carbonized.

J. Radcliffe (B. P. 10075, of 1905) recovers the sulphocyanide from the spent liquor and at the same time makes this innocuous by the following treatment. The neutralized (or slightly acid) liquor is run into a tank, together with a regulated quantity of copper salt solution, in a continuous manner. If the copper salt is in the cupric state, sufficient sulphurous acid must be added to effect its reduction to the cuprous state. The precipitate of cuprous thiocyanate formed is separated by filter-pressing, and by means of alkali it is converted into Cu_2O and marketable cyanogen compounds. Any copper present in the filtered liquor is removed by precipitation, either by means of lime or an alkali, or of metallic iron, and is then discharged in an innocuous state. It has a beneficial effect when added in the "bacterial treatment" of sewage.

Bower (B. P. 2918, of 1882) recovers from the waste still-liquor *ferrocyanide*, by neutralizing it with acid and thus precipitating Prussian blue. (*Cf.* Grossmann's process, *supra*, p. 1052.)

5. *Gases and Vapours given off in the Saturator.*

The gases escaping from the saturator consist of carbon dioxide, sulphuretted hydrogen, sometimes a little hydrocyanic acid, a small but very perceptible quantity of hydrocarbons, and perhaps also of sulphuretted organic compounds; all of them mixed with a large quantity of steam.

If this gaseous mixture were allowed to escape freely into the atmosphere, the nuisance would be altogether intolerable. It is bad enough if only a small proportion of it finds its way outside the works; even then the nuisance may be perceived at a distance of half a mile or more. Nor can the offenders easily evade detection; the smell of these gases is easily recognizable by its peculiarity. The public have a special dread of it, and thus any escape of this kind is sure to be soon traced to its origin and is fruitful of complaints.

Dr Ballard (*Report of the Medical Officer to the Local Government Board* for 1878, p. 131) expresses himself as follows about this matter:—"Medical men are usually ready to certify that the effluvia are injurious to public health, probably referring to the effects produced on those who are exposed to their influence in a diluted form, to the operation of the sulphuretted hydrogen as a poison. The public also readily believe that an atmosphere even slightly thus contaminated is dangerous to live in. It is certain that exposure to the diluted effluvia from sulphate-of-ammonia works does in many persons induce feelings of depression, headache, loss of appetite, nausea or vomiting, and sometimes some oppression of the breathing."

These gases and vapours are the chief source of complaints of nuisance, and from this cause (as well as from the preceding one) legal proceedings have been several times taken.

In some cases it seems sufficient to discharge these gases, etc., from the separator into a tall *chimney-shaft*. Especially where they can be first brought into communication with hot furnace-gases, this seems to suffice for removing the nuisance, as is proved by some works in Manchester, where shafts of 180 and 196 feet serve for this purpose. Where the liquor is worked up at the gas-works themselves, there is never any difficulty of that kind, as the immense volume of highly heated gases coming from the retort-fires is far more than sufficient to burn and dilute all effluvia from the ammonia-plant.

According to a communication from Mr Heuss, many German coke-works take the gases from the saturators directly into the ovens, by a pipe by which the gases are aspirated from the coke-ovens, so that they are ultimately burned in these, and the products of combustion are removed by the chimney.

But in other cases, where there is no very tall chimney-shaft,

or even with a tall shaft but an unfavourable conformation of the country, a thorough *combustion* of the gases must be aimed at. This is ordinarily done by carrying them by a pipe from the saturator into the side of the boiler fire, or under the fire-grate, or sometimes into a fire specially kept up for this purpose. But unless care is taken to remove the large quantity of watery vapour contained in the gases, the object in view will be only partially attained, or even quite frustrated by the vapours extinguishing the fire. It should therefore never be neglected to provide means for condensation. At some works the pipe which conveys the gases is continued into a worm, passing through a tank filled with gas-liquor or with water for feeding the steam-boilers, which are thus heated up previous to use. At the Plymouth gas-works an 8-inch pipe from the saturator is first carried beneath the floor on which the sulphate is dried, and thence runs along the surface of the ground, where it is bent upon itself, for a distance of about 500 feet, in the course of 290 feet of which it is played upon by jets of water flowing from a perforated pipe above it. At the Stampshaw works the 8-inch pipe from the saturator is first carried round the outside of the building at the eaves, and then enters a worm-condenser. At Illingworth's works at Bradford special care is taken to remove the watery and any other condensable vapours, as the sulphuretted hydrogen is there utilized for the manufacture of sulphuric acid. The gases are first conducted into a chamber made of an old boiler, through which the pipe conveying the liquor to the Coffey still passes, and they thus serve to warm the liquor; then by a pipe to two iron towers, divided by partitions springing at opposite sides alternately in such a way as to make a tortuous passage for the vapour; and, lastly, from these towers through a long series of vertical iron pipes, bent upon themselves in the same manner as a continuous condenser, such as is used in gas-works, water being made to flow continually down the outside of the pipes from a perforated water-pipe above. Other means for cooling the gases, and condensing the watery vapour therefrom, will be mentioned when describing in detail some of the varieties of plant seen by myself.

The condensed liquid, if not quite cold, may by itself cause a nuisance, and should therefore be cooled down before discharging it into a public drain.

The *combustion of the dried gases* is usually carried out by making them pass through a small coke-fire; and the sulphurous acid produced by the combustion of the sulphuretted hydrogen is usually discharged with the fire-gases up the chimney, and thus thrown away. Sometimes the gases are burned by themselves, *e.g.*, at Messrs Forbes & Abbott's works at Old Ford, where they enter by a 1-foot square opening into a small firebrick chamber and thence into a firebrick flue, about 15 feet long, 2 feet 6 inches wide, and 3 feet high; air is supplied by a small circular hole in an iron plate near the entrance of the gas, and the gases are ignited. Once the chamber and flue are red-hot, there is no fear of the gas being accidentally extinguished without relighting. The heat thus generated is then utilized for heating steam-boilers, which are said to have lasted for 14 years without receiving any injury by corrosion from the acid gases. The products of combustion, containing a large proportion of sulphur dioxide, are sent up the chimney-shaft.

Chateau[1] describes the apparatus used at Arcueil for deodorizing the gases evolved in the manufacture of sulphate of ammonia. They are aspirated by a fan-blast through a coke-column, 17 feet high, in which is spread a mixture of ferric oxide and calcium sulphate, constantly moistened by a solution of ferrous sulphate. Here ammonia and carbonic acid are retained [?]. The gases on issuing from the fan-blast pass over a thin layer of camphor and then into a combustion-furnace constructed by M. Perret. The grate-bars of this furnace are only $\frac{1}{24}$ inch apart, and are so deep that they can be made to dip into a water-basin in order to cool them and retain their shape. The gas enters in the narrow space between the water-basin and the grate. The latter is charged with anthracite dust, which is partly carried away by the gaseous current, but it is completely burnt in zigzag flues, made of fireclay flags, which soon attain a white-heat. At this high temperature hydrogen sulphide, ammonium sulphide, cyanogen compounds, and any other deleterious gases are completely burned, air being admitted by special openings for this purpose. The strong heat generated is employed for firing a steam-boiler. The apparatus is in regular operation, and is said to give very satisfactory results.

[1] *Bull. Soc. Chim.*, xxxvi., p. 195.

It should not be forgotten that the sulphurous acid discharged from a chimney may itself become a nuisance—no doubt much less than that which the sulphuretted hydrogen would have produced, but still sufficient to give rise to complaints. Besides this it may sometimes happen that the sulphuretted hydrogen is but imperfectly burned, and that enough of it escapes to create a nuisance.

All this can be overcome by one of two ways—either absorbing the sulphuretted hydrogen by some means, or burning it and *utilizing the* SO_2 *to form sulphuric acid.* The latter process has been in practical operation for several years past, first at Mr Illingworth's works at Frizinghall, near Bradford, then at Messrs Spence's works at Birmingham, and probably elsewhere. The gas is burned in a firebrick chamber, 12 feet long, 3 feet deep, and $4\frac{1}{2}$ feet wide, into which at one end the gas (previously carefully dried) is admitted by a pipe. There is a small air-opening close by. The products of combustion must pass through several pigeon-holed walls built across the chamber, in order to mix the gases and make the combustion perfect. They then play round the usual nitre-pots, and the mixture of SO_2, steam, nitrous fumes, nitrogen, CO_2, surplus air, etc., is carried into ordinary vitriol-chambers. If the combustion-chamber is once properly heated, the gas keeps lighted and the combustion proceeds satisfactorily; but when the work is stopped, for instance on Sundays, the heat of the chamber is maintained by a small coke-fire, burning on a grate just below the entrance of the gas-pipe.

It cannot be doubted that this process is entirely successful in removing all nuisances; but the presence of carbonic acid, etc., in the gases, is very injurious to the acid-forming process, and it seems doubtful whether there is, under ordinary circumstances, much profit to be made out of it. But it must be said to have answered its purpose if it effects the removal of the nuisance from the waste gases, even without any profit accruing from the process.

A much more profitable process than burning sulphuretted hydrogen for the manufacture of sulphuric acid is that of burning only the hydrogen and obtaining the *sulphur in the free state.* The only process of this kind which need be noticed here is that of C. F. Claus (B. Ps. 3606, of 1882; 5070

and 5958, of 1883), which, in connection with its application to the recovery of sulphur from the "tank-waste" of Leblanc alkali-works, has been thoroughly worked out, especially by Messrs Chance, of Oldbury. A complete description of this process is given in the author's *Sulphuric Acid and Alkali*, 2nd edition, vol. ii., pp. 894 *et seq.*, to which we must refer the reader for all details; only mentioning that the process consists in mixing the gas containing sulphuretted hydrogen with a quantity of air containing as nearly as possible the proper quantity of oxygen to produce the reaction $H_2S + O = H_2O + S$, and passing this mixture through a "Claus kiln," that is, a large iron cylinder lined with firebricks and partially filled with red-hot oxide of iron (pyrites cinders), which acts as a "catalytic substance." The issuing mixture of sulphur vapour, steam, nitrogen, and some undecomposed sulphuretted hydrogen is cooled down to recover the sulphur in the liquid or solid form, and the gases are eventually passed through a purifier before issuing into the atmosphere. A Claus kiln of 25 feet diameter furnishes from 15 to 20 tons sulphur in six days; about 85 per cent. of the sulphur is recovered, partly as block sulphur, partly as "flowers."

We shall here give only the description of a Claus plant specially erected for gas-works, at Leicester,[1] and serving for a weekly production of 35 or 40 tons sulphate of ammonia. The dried gases from the saturator (whose heat has been utilized for heating-up fresh gas-liquor) are conducted by a 6-inch pipe, *a*, (Fig. 300), into the kiln A. This is composed of an iron shell, with 18-inch brick lining, 3 feet wide and 5 feet long inside. A perforated partition, *c*, causes an intimate mixture of the gas and the air entering at *a* and *b*. The inner chamber, with an area of 3 feet × 3 feet, is filled with lumps of oxide of iron, containing a little manganese, 1 to 1¼ inch diameter. The sulphur generated here is deposited in chamber B, divided in the manner shown in the plan. From B the residual gases traverse a flue, E, 2 feet 6 inches wide and 58 yards long, in which are inserted a number of baffle walls, to within 12 inches of the bottom of the flue. At the end of flue E, which is in the form of a hollow square, the scrubber C is attached, 24 feet high and 4 feet diameter, packed with

[1] *Alkali Report*, No. 23, p. 81.

limestone over which water flows; here sulphuric acid and probably also some sulphuretted hydrogen are arrested, the remaining H_2S passing on to the open oxide-of-iron purifier D, 12 feet 10 inches square. On the bottom grids of this, coke is placed to take out any moisture that may remain; on the second grids oxide of iron to the depth of 3 feet 6 inches; the CO_2 freed from sulphur compounds passes away into the air. The apparatus C and D are decidedly necessary, as without them the gases from Claus kilns show acidities up to 12 g. SO_3 per cubic foot (*Alkali Report*, No. 23, p. 71).

In the *Thirty-sixth Alkali Report*, pp. 181 *et seq.*, experiments

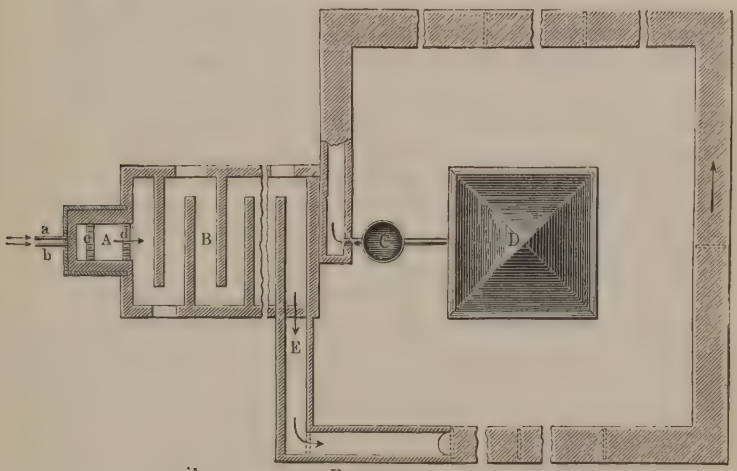


FIG. 300.

are described to adapt the Claus sulphur recovery method to the Scotch conditions by supplying a jacket of waste heat to the kiln to promote reaction, or at least to prevent loss of heat by radiation. Large scale experiments of the same class are described in the *Thirty-eighth Report*, pp. 148 *et seq.*, and it would seem that this modification answers very well for the treatment of dilute gases.

Van Eyndhoven (Ger. P. 170554) interposes between the saturator and the Claus kiln, first, a cooler for the condensation of steam into water, secondly, a cyanide washer.

Carpenter and Claus (*J. Soc. Chem. Ind.*, 1904, pp. 577 *et seq.*)

have made an extended investigation of the reactions in the Claus process. Apart from the well-known reactions:

$$(a) \quad 3S + 2H_2O = 2H_2S + SO_2$$

and

$$(b) \quad H_2S + O = H_2O + S,$$

others may occur which explain the facts even better in a thermochemical direction, viz.,

$$(c) \quad 3H_2S + 3O = 2H_2S + SO_3 + H_2O$$

and

$$(d) \quad 2H_2S + SO_2 = 3S + 2H_2O.$$

On the foundation of many experiments, also on the large scale, observations at factories, and calculations, the authors try to fix the conditions prevailing in Claus kilns, the conditions influencing the yield of sulphur and the part played in the process by ammonia. Ammonium sulphide is never found, but sometimes sulphite and sulphate, as well as thiosulphate and polythionates. Some samples of recovered sulphur contain so much ammonia that it must be removed by washing before burning the sulphur for the manufacture of vitriol. Hydrocyanic acid greatly reduces the yield of sulphur, the NH_3 is formed from it by the reaction:

$$HCN + H_2O = NH_3 + CO.$$

Where the output is too small to make the Claus process available, and the disposal of the gases to a vitriol plant is impossible, the treatment by combustion and *absorption by calcium carbonate* is sometimes adopted with great success (*Thirty-fourth Report of the Alkali Inspectors*, pp. 29, 114, 115; *Thirty-fifth Report*, pp. 117, 118; *Thirty-sixth Report*, pp. 25, 79, 153). The gases, after being subjected to thorough condensation to remove aqueous vapour, pass to a furnace designed especially to act as an "accumulator" of heat, where complete combustion of the H_2S to SO_2 is effected. With gases containing 20 per cent. by volume of H_2S, the flame of a large gas or jet is sufficient to initiate and maintain combustion at the end of the pipe, bringing the foul gases to the furnace, the reaction being made complete by prolonged travel of the gases over the surface of brick and tiles kept at a bright red-heat, Provision is made for supplementary air being admitted at various points in the furnace, so that no vapour of sulphur may pass unoxidized. Attention to this point is of the first

importance, else sulphur solidifies in the later portions of the apparatus, and the disorganization, once commenced, rapidly increases as the primary supply of air is checked by the diminution of draught at the furnace. The gases, after subsequent cooling to air temperature, pass to the bottom of a tower packed with limestone and fed on the top with a shower of water, *e.g.*, by the tumbling-box arrangement used for Gay-Lussac towers in the condensation of hydrochloric acid, etc. (Lunge's *Sulphuric Acid and Alkali*, 3rd ed., vol. i., p. 592). Under these conditions the SO_2 is fixed by the CaO of the limestone, and issues from the bottom of the tower in solution as calcium bisulphite.

At one of the Metropolitan works the limestone scrubber consists of a wooden structure made of 1½-inch tongued and grooved boards, 5 feet 6 inches square and 21 feet high. Layers of Derbyshire limestone in good-sized pieces are supported on fine stout wooden gratings, the layers of stone being some 9 inches deep. Manholes for recharging the trays with fresh stone as this wastes away are provided above each tray. A tumbling-box for flushing with water is fixed inside the scrubber at the top, at which point the neutralized gases leave the apparatus for the draughting chimney. The inlet and outlet pipes are of cast-iron, but lead would perhaps be better, as there is some little action of the gas on the iron. The average acidity of the furnace gas on entering the scrubber at that works is 41·40 grains SO_3 per cubic foot, on leaving the scrubber 0·81 grains, showing a condensation of 98·05 per cent. On the average of all the works the condensation may be put=95 per cent.

After several years' experience of this process, the Alkali Inspectors state the following precautions as absolutely necessary for success:—

1st. There must be command of draught at the furnace, *i.e.*, the suction at the condenser outlet must be adequate to supply this at all times, else sublimation of sulphur with attendant evils will occur. Possibly air might be supplied to the furnace under slight pressure, equal to that of gases from saturator.

2nd. Adequate and complete cooling of the gases before the furnace and also afterwards. If the gases enter the limestone tower above 38° C., containing as they will excess of

oxygen with sulphur dioxide, the formation of $CaSO_4$ is promoted. This forms a protective crust on the surface of the limestone, thus impeding the action of the latter on the SO_2. The condensation of water from a hot gaseous mixture, containing steam + SO_2, causes great corrosion of the iron pipes, especially at the chaplets of the pipes, which are of wrought-iron. Here lead should be used for the pipes, ensuring the delivery of the gas at the tower at a temperature not above 38° C., or lower if possible.

3rd. Cast-iron does not seem the best material for use in the construction of the tower. Wood planks tongued and grooved last well, even in summer heat, and cement towers have stood well.

4th. The supply of water is best arranged in two forms, one constant, the other intermittent (by flushes), at least in the case of limestone which is not a porous body, and holds no reserve of condensing power within itself like coke. But if hard chalk is used, the intermittent flush, at no great intervals, is admissible.

Wilton (Manager of the Beckton Tar and Ammonia Works) in his English patent No. 15468, of 1901 (*Chem. Trade J.*, 1901, vol. 29, p. 372), describes a process whereby the H_2S is burned in a suitable furnace *with an excess of oxygen*. The hot mixture of SO_2, free O, N, etc., is passed through iron scrap, contained in towers fed with water or mother-liquor from the sulphate of iron crystallizing tanks. Thus a concentrated solution of sulphate of iron is produced, which is allowed to crystallize in suitable vessels. Or else the towers are packed with limestone, in which case a solution of calcium sulphate is formed, which may be run to waste as a practically inoffensive fluid, and such a limestone tower may be placed behind the scrap-iron towers, in order to catch the SO_2 escaping from these.

Instead of burning the sulphuretted hydrogen, it is frequently, especially at smaller works, *absorbed in a purifier, charged with lime or oxide of iron*. For this purpose the condensable vapours must be equally removed by cooling; and the dried gases are then passed into purifying-apparatus, constructed exactly like those used at the gas-works, and for the same purpose, as shown in Fig. 301. They are cast-iron boxes, provided with a rim at the top for a hydraulic lute, into which dips the flange

of the cover. The gases enter at the bottom and pass through trays, usually made of wood, on which the purifying-material is spread out in a layer of 3 or 4 inches. The purified gas finds its way out through a pipe from the upper portion of the box. Several such boxes are usually combined, so that they can be worked in regular rotation; that box receiving the fresh gases which has been the longest time at work, and that receiving the gases just before escaping into the atmosphere which has been last charged with fresh material. Such boxes are made, for example, from 10 to 20 feet square and from 2 to 4 feet high; they may also be made of brickwork, but they should not be made of wood, as it is difficult to keep them tight in that case.

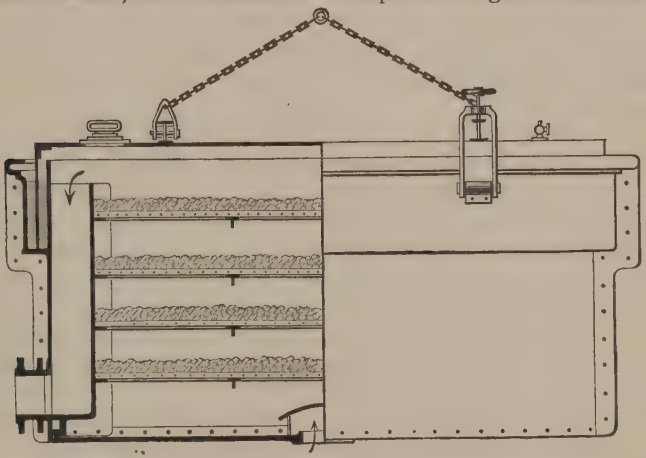


FIG. 301.

Moreover, the heat developed in the absorption of H_2S may injure the wood, and for this reason it is also preferable to substitute perforated iron or wire-gauze trays for those made of wood.

Sometimes the absorbing-material used is lime; but this is anything but rational. The lime is wasted once for all, and the spent lime ("blue-billy") is a fresh nuisance, which may cause considerable trouble. A much better material is that used at nearly all gas-works, namely, the hydrated peroxide of iron, generally mixed with sawdust. This material, when it has ceased to be active, can be regenerated by simple exposure to the air, which causes the iron sulphide to be converted into a

mixture of ferric hydrate and free sulphur; and when the sulphur has accumulated to such an extent that the material becomes definitively useless for absorbing H_2S, the "spent oxide of iron" is a valuable material for the production of sulphuric acid, so that its sulphur is turned to a useful purpose.

Sometimes a fan-blast or an injector of some kind is used for driving the gases through the purifiers. In other cases they are connected with a high chimney; but this may cause the purifiers to be left unnoticed for some time, which cannot happen with open purifiers.

If on reviving the oxide, ferrous sulphate is formed, a sufficient quantity of lime must be added to decompose this.

This process is best adapted for small works, up to 300 tons production per annum. At larger works the space required by the purifiers and the labour of reviving the oxide cause great inconvenience.

For this purpose the gases must be deprived of most of their steam, as well as when burning, since otherwise the oxide becomes too dense and does not allow the gases to pass (*cf.* the contrivances described, p. 1095). A partial cooling of the gases can be produced by blowing cold air into them by means of an injector; this air afterwards assists in oxidizing the sulpnide in the purifiers, so that these work continuously. Otherwise the purifiers are worked intermittently, by passing through alternately gas and air, making the change every 3 or 6 hours. Care must be taken to keep the valves in good order, to protect the men, employed for turning over the oxide in the purifiers during the blowing in of air, against the entrance of foul gas intended for another purifier.

The *Alkali Inspectors' Report*, No. 32, p. 16, gives the following analyses of spent oxide—(*a*) from intermittent, (*b*) from continuous work:—

	a	*b*
Water	4·65	24·90
Free sulphur (calc. for dry mass)	73·90	59·80
Sulphur as soluble sulphates	1·00	0·95
Sulphur as insoluble sulphates	traces	0·40
„ „ FeS	1·20	1·85
	80·75	87·90

Many other analyses are given in *Report* No. 33, pp. 16 and 17.

According to *Report* No. 42, p. 23, the opinion of practical men is generally in favour of applying the oxide of iron in the form of a conical heap on a concrete floor, the foul gases being introduced below by a simple gas-distributing device—rather than in that of a specially constructed purifier with retaining walls. The occurrence of fouling in the mass is more easily detected and rectified, and there is less labour in spreading the material when finally fouled for revivification.

We here notice briefly some other processes for dealing with the foul gases.

Young (B. P. 1310, of 1880) conveys the ammoniacal vapours, evolved without using lime, not through a saturator, but along with air through a fireplace, where the ammonium sulphide is partly burned into sulphite and partly into sulphate, which are conveyed into a suitable condenser. The ammonium sulphite is converted into sulphate by passing a current of heated air through the solution (as previously proposed by Laming). Since the gas-liquor never contains enough sulphides to convert all the ammonia into sulphate, sulphur dioxide is mixed with the products of distillation before or after they have passed through the fire, or else the condensed liquid is saturated with sulphurous or sulphuric acid. This process is evidently altogether analogous to that patented by Messrs Addie for blast-furnace gases: it has the disadvantage, however, that at the high temperature employed much ammonia will be burned, and that the condensation of the highly heated ammonia compounds diluted with air is not an easy matter.

Hemingway (B. P. 9432, of 1899) burns part of the H_2S evolved in the manufacture of ammonium sulphate and scrubs the SO_2 produced in a coke-tower, to the upper part of which ammonia is admitted, passing on the surplus SO_2 to a second tower. The ammonium sulphite is decomposed by ferrous sulphate into a mixture of ferrous sulphite and ammonium sulphate, which in a third coke-tower is treated with another part of the H_2S originally evolved. In this tower FeS and S are deposited as solids, and the solution of ammonium sulphate is run off from the bottom. *Cf.* also *Alkali Inspectors' Reports*, No. 35, p. 142, and No. 36, p. 172, concerning experiments on a continuous removal of sulphuretted hydrogen by means of manganese salts and oxygen.

Hemingway (*Z. angew. Chem.*, 1904, p. 1026) treats the H_2S escaping from the saturator for the recovery of sulphur.

Lessing and Wilton (B. P. 4766, of 1905) recover pyridine bases from the waste gases (or from crude gas-liquor) by washing them with heavy tar oils, suitably with addition of crude phenols.

Becker (Ger. P. 196015) removes the H_2S and HCN from the gases escaping from the saturators by washing them with water and adding this to the waste liquor, which contains free lime and thus saturates the H_2S and HCN.

Feld (Ger. P. 192533) absorbs H_2S from gases by means of metallic compounds, *e.g.*, oxides of manganese, which yield insoluble sulphides. These are afterwards heated with solutions of ammonium salts, whereby the metallic compounds are regenerated and the H_2S and NH_3 are expelled.

The Smell arising from the Evaporation of the Sulphate Liquors, where strong acid is not used, has been already mentioned. This smell has been likened to the odour from ill-kept pigsties, and sometimes this vapour may be a nuisance at a distance of 200 yards or more—nearly as much as the saturator-gases. To obviate it, steam should be driven through the saturator for 20 minutes or half an hour before running off the finished solution into the evaporating-pans; and this steam should be carried off and condensed in the usual way (*Dr Ballard's Report*, p. 135; cited above, p. 1086).

It stands to reason that all processes for dealing with the sulphuretted hydrogen are much more easily carried out with the gases from continuous stills, like Grüneberg's, Feldmann's, etc., than with those from intermittent stills.

Very interesting are the statements on the results of dealing with the foul gases, sulphuretted hydrogen, etc., from ammonia-works, found in the *Reports of the Alkali Inspectors*. We here quote those found in the last published *Report*, No 43, for 1906, pp. 67, 73, 79, 96, 103, 113, 125, 141, 153; I combine these into the following table:[1]—

[1] The figures given in the last *Reports* were not yet in my hands when that table was printing, but they do not to any material extent differ from those here given.

Method of Destruction of the Foul Gases.	Percentage of Ammonia dealt with by the various Methods in District.								
	No. 1.	No. 2.	No. 3.	No. 4.	No. 4a.	No. 5.	No. 6.	No. 7.	Scotland.
By combustion	0·5	...	...	...	5·9	...	23·0	2·8	8·8
To vitriol chambers	...	11·8	...	27·1	20·0	...	6·7	67·9	...
By Claus process	...	16·4	2·0	13·4	26·5	15·2	5·3	12·0	13·0
In oxide-of-iron or lime-purifiers	89·1	32·9	39·8	36·4	47·6	30·5	64·6	8·9	70·0
To hydraulic main	...	...	...	...	...	...	...	0·6	...
By treatment with gas-liquor and subsequent combustion	...	36·9	...	...	...	3·7	...	...	...
By combustion of the H_2S and arrest of the SO_2 in limestone towers	...	...	...	...	...	1·5	0·4	7·8	...
By various processes	...	...	...	23·1	...	42·9	...	...	...
Retained by metallic salts	10·4	2·0	58·1	...	...	...	...	...	7·7
No H_2S generated, by the use of special processes	...	...	...	...	...	6·2	...	...	...

According to the *Alkali Inspectors' Reports* (*e.g.*, No. 28, pp. 57, 66, 87, etc.), the majority of works, in some districts two-thirds, burn the H_2S for the production of sulphuric acid, usually by introducing it into pyrites-burners; others mostly use oxide-of-iron purifiers, a few the Claus process, and some burn the H_2S into SO_2, which escapes into the air. In one of the largest districts, producing 39,400 tons sulphate per annum, in 1893 (*Alkali Report*, No. 30, p. 100) 60·8 per cent. of the H_2S was converted into sulphuric acid, 11·6 into sulphur by the Claus process, 9·5 removed by oxide of iron, 18·9 burned and allowed to go into the air. In another district in 1894 (*Report* No. 31, p. 15), two works employed milk-of-lime and ferrous sulphate, two employed the H_2S for removing arsenic from sulphuric acid, 71 burned it and sent the SO_2 into the air, 23 made sulphuric acid from it, 24 employed the Claus process, 276 oxide-of-iron purifiers, 51 lime-purifiers.

According to *Report* No. 31, p. 98, the *cost* of removing the H_2S was as follows:—With oxide-of-iron purifiers in 7 cases: 2s. 6d., 1s. 6d., 3s. 4d., 3s., 5s. 5d., 7s. 1d., and 3s. 6d., including interest and amortization; with the Claus process in 5 cases: 8d., 1s. 1d., 11½d., 1s. 1d., 1s. 1½d. In no case was a real profit made.

Stevenson[1] gives a calculation for the conversion of sulphuretted hydrogen from gas-liquor into sulphuric acid. In the course of a year 1977 tons of sulphuric acid (of what strength?) was made, and for this was used: 1023 tons pyrites 40 per cent., 99½ tons nitrate of soda, 342½ tons coke, £291 wages, £602 repairs, £300 5 per cent. interest on £5000; also the H_2S from 32,549 tons gas-liquor. Over and above the interest, a profit of £330 was made.

Concentration of Ammonium Sulphate Solutions.

We have spoken of this operation several times in the preceding description of various processes. Here we will only mention that it is generally carried out in leaden pans, heated by leaden steam-coils. Iron is not a suitable material in this case, as it is acted upon by ammonium salts, especially at higher temperatures, owing to the escape of a little free

[1] *Gas World*, 1895, p. 705.

ammonia. Even if this action were so slight that it would do no serious injury to the apparatus (and this would most easily happen to wrought-iron steam-coils and the like), the iron would cause a discoloration of the ammonium salts, and reduce its commercial value. It is doubtful whether this could be entirely avoided by the proposal of P. S. Brown (B. P. 804, of 1878) to use boiling-pans made of iron, taking care to keep the liquid always slightly alkaline.

Manufacturing Sulphate of Ammonia otherwise than from Ammoniacal-Liquor.

A somewhat considerable quantity of sulphate of ammonia is recovered by washing spent oxide of iron from gas-purifiers and evaporating the washings. This salt is, however, very impure (*vide infra*).

Fogarty (B. P. 13747, of 1887) produces ammonium carbonate by burning "alkalized coal" in an atmosphere of air, steam, and nitrogen, and allows it to be absorbed by a mixture of calcium sulphate and sawdust, from which afterwards the ammonium sulphate is obtained by lixiviation.

Roustan (Ger. P. 46135) purifies coal-gas by a mixture of liquid calcium oxychloride, or calcium chloride and magnesia, with slaked lime and coke. The NH_3 condenses therein as carbonate, which is driven out by heating to a red-heat, and is absorbed in sulphuric acid, or condensed by cooling.

Eastman (B. P. 10192, of 1888) mixes coal-tar, heated to 37° C., with calcium sulphate and water; the aqueous liquid separating contains ammonium sulphate. F. H. Davis (B. P. 101976, of 1890) employs a similar process, but substitutes for the calcium sulphate a solution of copper or zinc sulphate. Both inventors evidently principally aim at the production of purified tar. The ammonia recovered will be hardly worth the expense.

Properties of Commercial Sulphate of Ammonia.

The properties of pure ammonium sulphate have been described, p. 959. The commercial salt, when made with sulphuric acid free from arsenic and iron, should be white, or at least light grey. The salt formerly made by direct satura-

tion of gas-liquor with sulphuric acid was, of course, dark grey or brown; and even that now made by distilling ammonia into sulphuric acid has a dark colour, unless precautions are taken against this by the mode of saturating the liquor (p. 1067). It must also be noted that the sulphate made in the more perfect apparatus, as those of Grüneberg, Feldmann, and others, is much less liable to be coloured, because the tarry impurities are mostly condensed in the dephlegmating-columns. But even then the sulphate may, after some time, assume a yellow colour from iron salts gradually accumulating in the saturator; this is avoided by cleaning the latter out from time to time. Sulphide of arsenic also causes a yellow colour, and for this reason many English manufacturers employ brimstone-acid (p. 1077); but even in Germany, where pyrites-acid is exclusively used, the sulphate is not usually yellow, partly because sulphuric acid made from purer pyrites is generally employed, partly because the arsenious sulphide can be skimmed off during saturation, sometimes with special additions (p. 1078).

Sometimes the sulphate shows a more or less pronounced *blue* colour, which gives trouble in disposing of it. The first mention of this is found in *Chem. Zeit. Rep.*, 1866, p. 282, but this subject has only quite recently evoked much attention, and has been treated at length by the Inspectors of Alkali Works, in their annual reports for the years 1905 and 1906, especially by Mr Linder (*Rep.*, No. 42, pp. 51-62). Mr Carpenter, in No. 43, p. 30, sums up the results arrived at. The blue colour is caused by an insoluble *ammonium ferrous ferrocyanide*, precipitated among the separating crystals of ammonium sulphate, and this will take place, if *local alkalinity* occurs at some part of the separator, especially in the neighbourhood of the pipe distributing the vapours containing volatile ammonium salts, ammonium cyanide being one of these. The first stage consists in the formation of ammonium ferrocyanide, which occurs by the separation of hydrated iron sulphide or oxide in suspension from the mixture in the separator, owing to that mixture becoming neutral or alkaline. This formation is favoured by low temperature, as the solubility of hydrocyanic acid is thereby increased; once this is fixed as ferrocyanide, no amount of subsequent boiling under ordinary pressure will remove it. In the second stage, with access of ferrous salts in acid solution, a

white precipitate of ammonium ferrous ferrocyanide, insoluble in acid, is produced. This is not noticed on fishing out the crystals of ammonium sulphate, but on continuous exposure to the air the ferrous salt, a third reaction takes place, viz., oxidation to ferrocyanide, *i.e.*, Prussian blue. It is easy to examine the sulphate for the chance of turning blue on keeping by testing a sample of the fresh salt with hydrogen peroxide or another oxidizing agent.

Hence we may take it for certain that local alkalinity, coupled with low saturator temperature, are the conditions favouring the formation of blue sulphate. Priming over of ammoniacal liquor from the stills would induce both these conditions, but they can exist without priming having occurred. We may take the following equations as representing the three stages:—

(*a*) $6NH_4Cy + FeS = (NH_4)_4Fe(Cy)_6 + (NH_4)_2S$.
(*b*) $(NH_4)_4Fe(Cy)_6 + 2FeSO_4 = Fe_2Fe(Cy)_6 + 2(NH_4)_2SO_4$.
(*c*) $Fe_2Fe(Cy)_6 \rightarrow Fe_3(Fe(Cy_6)_2 \rightarrow Fe_4(Fe(Cy_6)_3$.

Cf. also Bailey, *J. Gas Lighting*, 1907, p. 522.

The ammonium sulphate, as it comes from the saturators, is often merely drained and sold in the moist state; in this case it will be very perceptibly acid. This can be avoided by carefully washing it, with very little water, on the drainer, but more easily by employing a centrifugal machine lined with lead, in which also the washing can be performed.

The drying of the salts, if necessary, can be effected in stoves, heated by the waste heat of some flue or by exhaust steam from an engine, or on open floors or plates heated from below.

Ammonium sulphate is always sold according to its percentage of nitrogen or ammonia. Chemically pure salt would test 21·21 per cent. N, or 25·75 per cent. NH_3, and even commercial salt sometimes tests 24 or 25 per cent. NH_3. The analytical processes serving to ascertain the percentage of ammonia will be mentioned later on.

In the English trade the strength usually stipulated for between buyer and seller is 23 per cent. NH_3. As the manufacturers found that they could get up to $25\frac{1}{2}$ per cent., they brought this down to 23 per cent. by adding common salt or

sulphate of soda; but some buyers object to this in the sale-note. (Watson Smith, private communication.)

In England it is usual to quote the strength of ammonium sulphate as percentage of ammonia, in Germany as percentage of nitrogen.

The following table will help to quickly reduce either of these terms to the other:—

Table for comparing the percentage of Nitrogen and that of Ammonia.

N.	NH_3.	N.	NH_3.	N.	NH_3.	N.	NH_3.
0·1	0·12	0·9	1·09	8	9·71	16	19·43
0·2	0·24	1	1·21	9	10·93	17	20·64
0·3	0·36	2	2·43	10	12·14	18	21·85
0·4	0·49	3	3·64	11	13·35	19	23·07
0·5	0·61	4	4·86	12	14·57	20	24·29
0·6	0·73	5	6·07	13	15·78	21	25·40
0·7	0·85	6	7·29	14	17·00		
0·8	0·97	7	8·50	15	18·21		

A most objectionable impurity in ammonium sulphate is *ammonium sulphocyanide* (thiocyanate). This is scarcely found in such salt as is obtained by distilling gas-liquor with lime and absorbing the gas in sulphuric acid; but it may occur in the salt obtained by direct saturation of gas-liquor with acid (p. 964) and it is regularly found in the salt which is made by washing spent oxide of iron from purifiers and simply evaporating the washings (p. 887). The latter product contains frequently 25, sometimes even up to 91 per cent. of sulphocyanide.[1] Since this salt is very injurious to vegetation,[2] and lessens the value of ammonium sulphate, or even makes it quite unsuitable for manuring-purposes, such solutions from spent oxide ought never

[1] Esilman & Bell, *Chem. News*, xxxii., pp. 124, 197.

[2] The damage done to plant-growth by ammonium sulphocyanide (thiocyanate), which was considered a matter of notoriety, has been represented as slight by Mr Märker (Biedermann's *Centralblatt fur Agrikulturchemie*, 1883, p. 494). But the researches of P. Wagner (*ibid.*, 1873, p. 336), of C. Schumann (*ibid*, 1882, p. 332), and of C. Böhmer (*Wagner-Fischer's Jahresber.*, 1884, p. 324), on the contrary, fully prove the injurious action of the sulphocyanides on plants.

to be utilized by direct evaporation, but should be distilled with lime; from the residue calcium sulphocyanide may be extracted, and may be worked up into sulphocyanides, which have now become articles of commerce.—The detection of sulphocyanide in commercial sulphate is easily made by the well-known red colour which it gives with ferric chloride (*cf.* pp. 937 and 940).

P. G. Lloyd (*Chem. News*, 1908, vol. xcviii., p. 172) points out that for some years past commercial sulphate of ammonia rarely contains any appreciable quantity of sulphocyanides, but sometimes it contains organic compounds injurious to plant life, probably owing to their influence on the nitrifying organisms. Gas sulphate sometimes shows this action in special cases, but bone sulphate does not, although very strongly coloured. His assistant, Dr Bonelli, found a test for this. If 1 g. of the sulphate is dissolved in 5 c.c. water and strong ammonia added, an intense violet coloration is produced where the undesirable organic compounds are present, while no change occurs either with pure gas sulphate or bone sulphate. To detect sulphocyanides in the presence of those organic compounds, moisten 5 g. of the sulphate of ammonia with strong ammonia, dry in a water-oven, grind with 5 c.c. alcohol, filter, dilute the alcoholic filtrate with water, and test with ferric chloride, which gives the usual bright red coloration if sulphocyanides are present.

Applications.

Most of the ammonium sulphate is employed as a fertilizer; for the cultivation of beetroot especially it cannot be replaced by the cheaper nitrogen of nitrate of soda; hence the very large importation of this salt into Germany (*cf.* p. 1110). The action of ammonia as manure is slower that that of nitrate of soda, but all the more lasting. It is absorbed by the soil and retained even after large quantities of rain have come down, whereas nitrate of soda is washed out in this case, and its soda also renders the soil in the end too hard for tilling. According to the kind of crop and the conditions of clime and soil, either ammonium sulphate or sodium nitrate will be best to apply. On the whole, ammonia is preferable for potatoes; for wheat, rye, and oats, they are of equal value. The sulphate also serves for preparing the other ammonium salts, and sometimes for liquor ammoniæ, and for making ammonia-alum. In the manu-

From	1889	1894.	1895.	1896.	1897.	1898.	1899.
Gas-works	87,000	113,634	119,645	127,498	132,724	129,590	136,529
Blast-furnaces	5,500	10,075	14,588	16,511	17,772	17,935	17,963
Shale-distilleries	22,000	32,298	38,325	37,822	37,153	37,264	38,780
Gas-producers, coke-ovens, etc.	3,000	3,448	7,083	9,078	10,624	11,568	15,209
Total	117,500	159,455	179,641	190,909	198,273	196,357	208,184

From	1900.	1901.	1902.	1903.	1904.	1905.	1906.	1907.	1908.
Gas-works	142,419	142,703	150,055	149,489	150,208	155,957	157,160	165,474	165,218
Iron-works	16,950	16,353	18,801	19,119	19,568	20,376	21,284	21,024	18,131
Shale-works	37,267	40,011	36,931	37,353	42,486	46,344	48,534	51,338	53,628
Coke-oven works	10,393	12,255	15,352	17,438	20,848	30,732	43,677	53,572	64,227
Producer-gas and carbonizing works (bone and coal)	6,688	5,891	8,177	10,265	12,880	15,703	18,736	21,873	24,024
Total	213,726	217,212	229,316	233,664	245,990	269,114	289,391	313,281	325,228

facture of ammonia-soda, the sulphate is now mostly replaced by the cheaper concentrated gas-liquor (pp. 975 *et seq.*).

A 10-per-cent. solution of ammonium sulphate is employed to render tissues, papers, etc. non-inflammable.

A very important application for ammoniacal nitrogen seems to be in store for the manufacture of nitric acid from ammonia, by the invention of Ostwald and others.

Statistics on the Manufacture of Sulphate of Ammonia.

The table on p. 1106 gives the official statistics of the sulphate of ammonia produced in Great Britain (tons), according to the *Alkali Inspectors' Reports.*

The following table shows the amount of ammonium sulphate *exported* from Great Britain to other countries, expressed in units of 1000 tons:—

Year.	Germany and Belgium.	Spain.	France.	Java.	Holland.	United States.	British Guiana.	West Indies.	Other Countries.	Total.	Home Consumption.	Percentage of Exportation.	Percentage of Home Consumption.
1894	41·5	17·4	8·8	6·2	11·9	4·3	5·3	3·7	4·2	103·3	56	64·85	35·15
1895	40·3	22·2	7·3	5·9	7·1	11·6	6·2	2·4	8·7	111·7	67·8	62·23	37·77
1896	43·4	21	12·8	8·3	7	9·8	6·8	4·3	12·6	126	64·5	66·14	33·86
1897	55·2	27·2	23·1	6·8	9·8	8·9	4·9	4	13·1	153	45	77·27	22·73
1898	42·2	31·5	16	18·3	10·2	4·7	6·3	4·9	12·8	136·9	59·6	69·67	30·33
1899	33·6	38·3	10	13·6	8·4	8·2	5·2	4·8	18·13	140·2	65·3	68·22	31·78
1900	32·6	37·5	11·7	11·5	10·3	9·5	7·6	5·5	19·1	145·3	67·7	68·22	31·78
1901	41·6	36·9	6·7	14·2	(?)	10·6	(?)	(?)	(?)	150·2	63·5	70·29	29·71
1902	44·1	40·3	12·6	15·5	7·2	10·1	7·1	4·5	21·4	162·8	68·7	73·5	26·5
1903	35	43·6	9·6	19·3	7·9	8·4	7·8	3·6	27	162·2	61·8	73·6	26·4

According to *Forty-fourth Alkali Report* (p. 35), the exports of ammonium sulphate from the United Kingdom in 1906 were 201,500 tons; in 1907, 230,000 tons: the home consumption in 1906, 82,000 tons; in 1907, 87,500 tons. Japan in 1902 took only 4000 tons; in 1907, 64,000 tons.

Iron-works recovering ammonia from blast-furnaces in the United Kingdom are almost exclusively confined to Scotland, as only in special districts coal is hard enough to stand in the blast-furnace without crushing. The English works are confined to

Staffordshire. The production from shale distillation is entirely confined to Scotland. The most remarkable development concerns the coke-oven works, as is apparent from the above table, but England is still far behind Germany in that respect (*cf.* p. 907).

In District No. 2 (North of England), where liquor corresponding to 29,666 tons of sulphate of ammonia was distilled in 1906, but 0·17 per cent. of this was made into liquor ammoniæ. Fifty-seven works used continuous distillation, representing 99·7 per cent. of the liquor distilled; 8 small works used discontinuous distillation. This proportion is almost the same in the other districts, the proportion of liquor distilled by continuous processes being from 99·1 to 99·5 per cent. of the total.

The number of ammonia-works (sulphate, muriate, and gas-liquor) in the United Kingdom in 1906 was 536, in 1907, 554.

The production of ammonia in the United States, expressed in its equivalent of sulphate, according to *The Mineral Industry*, xv., p. 28, expressed in short tons of 2000 lb., has been:

	1898	1899	1900	1901	1902
Short tons . .	17,000	19,500	27,600	29,279	36,124
	1903	1904	1905	1906	1907
Short tons . .	41,873	54,664	65,296	75,000	89,000

At the present time about three-fourths of the ammonia comes from by-product coke-ovens.

The following table shows the imports, the total consumption and the average market price per short ton of 2000 lb. in the United States:—

	1899	1900	1901	1902	1903	1904	1905	1906	1907
Imports (short tons) . .	6,976	8,411	14,486	18,146	16,777	16,667	15,288	9,182	30,114
Total consumption (short tons) . .	26,476	36,011	43,765	54,270	58,650	71,331	80,584	84,182	119,814
Market price .	$50·29	$57·40	$55·16	$59·90	$62·10	$61·71	$62·92	$62·33	$61·93

The following estimate of the world's production of ammonium sulphate is given in *The Mineral Industry*, xvi., p. 31. The unit is metric tons = 2204·6 lb.

Country.	1902	1903	1904	1905	1906	1907
Great Britain . . .	225,300	230,200	241,500	264,400	279,900	331,220
Germany	135,000	140,000	173,000	190,000	235 000	287,000
United States . . .	33,000	38,000	50,000	60,000	68,000	81,400
France	40,000	52,000	43,000	47,300	49,100	52,700
Belgium and Holland .	38,000	35,000	39,000	24,200	30,000	55,000
Other European countries	45,000	45,000	48,000	55,000	55,000	88,000
Total . .	516,300	540,200	591,500	640,500	716,100	895,320

In 1907, according to the report of Bradbury and Hirsch, Great Britain produced over 316,000 long tons, of which 230,537 tons were exported.

N. Caro (*Die Stickstofffrage in Deutschland*, 1908, p. 18) gives the following table for the production of ammonium sulphate in Germany :—

Year.	At Gas-works.	At Coke-works.	Total sulphate.	Liquor ammoniæ.	Excess of importations of sulphate from abroad over exportations.
	Tons.	Tons.	Tons.	Tons.	Tons.
1897	14,000	70,000	84,000	...	30,492
1898	14,000	84,000	98,000	...	26,172
1899	15,500	84,500	100,000	...	27,315
1900	18,000	88,500	106,500	580	20,674
1901	20 000	113,000	133,000	720	34,866
1902	23,000	117,000	140,000	1180	36,509
1903	26,000	120,000	146,000	1630	29,576
1904	30,000	152,000	182,000	1680	24,468
1905	35,000	168,000	203,000	2425	27,416
1906	38,000	197,000	235,000	2500	...

In 1907, the total production of Germany amounted to 287,000 tons ammonium sulphate, of which 30,000 tons came from gas-works, 257,000 tons from coke-works.

The following figures show the importations and exporta-

tions of sulphate of ammonia for Germany during the last few years (from *Chem. Ind.*, 1908, p. 516):—

	1904	1905	1906	1907
	Tons.	Tons.	Tons.	Tons.
Importation	35,166	48,005	35,366	33,522
Of this from Great Britain . .	17,678	26,813	16,283	13,500
„ „ Austria . . .	12,293	14,519	15,686	16,524
Exportation	10,696	27,589	37,288	57,493
Of this to Belgium . . .	5,219	18,078	23,692	30,940
„ „ France	371	1,027	2,629	7,242
„ „ Italy	6	279	3,601	6,507
„ „ Netherlands . . .	1,345	1,167	4,691	11,756

Italy (*Chem. Ind.*, 1908, p. 523) produces about 5000 tons, and imports another 4000 tons, nearly all from England.

In *Chem. Trade J.*, xliii., p. 150, we find the following official statements for the production and importation of sulphate of ammonia in Italy:—

Year.	Productions.	Imports.	Total.	Year.	Productions.	Imports.	Total.
	Tons.	Tons.	Tons.		Tons.	Tons.	Tons.
1896	1,523	...	...	1902	3,440	5,501	8,941
1897	1,666	...	...	1903	3,686	5,367	9,053
1898	1,350	3,858	5,208	1904	3,837	6,975	10,812
1899	1,436	4,504	5,940	1905	4,124	5,201	9,325
1900	2,147	5,362	7,509	1906	4,820	9,738	17,558
1901	2,967	4,297	7,264	1907	...	14,942	...

CHAPTER XV

OTHER TECHNICALLY IMPORTANT AMMONIUM SALTS

Ammonium Chloride (Sal-ammoniac)

This salt formerly came from Egypt, and from the 13th century till late into the 18th this was the only source of ammonium salts available in Europe (apart from the direct use of putrefied urine in dyeing, etc.). In Egypt sal-ammoniac was made as a by-product in utilizing dried camels' dung for fuel.

The food of the camels to a great extent consists of plants containing a large amount of salt, and their urine contains some ammonium chloride ready formed. The principal portion is, however, only produced from the nitrogenous substances and the chlorides when burning the camels' dung dried in the sun. The soot formed in burning was carefully collected and subjected to sublimation in special factories (one of which, in the delta of the Nile, was visited by the Jesuit Sicard in 1720). Forty pounds of soot are said to have yielded about 6 lb. of sal-ammoniac.

In other countries, where dried dung is also used as fuel, it has been sometimes attempted to manufacture sal-ammoniac by mixing salt with the dung before burning it, and collecting the soot. This manufacture does not, however, seem ever to have had any considerable extension, except in India, whence large quantities of sal-ammoniac were formerly exported.[1]

In Europe sal-ammoniac is said to have been first obtained by the destructive distillation of oil-cake (a remarkably wasteful process!) and from the soot formed in the burning of coal.

[1] A detailed account of the manufacturing processes formerly used in Egypt and India for making sal-ammoniac is contained in *Chemistry as applied to the Arts and Manufactures*, London (Mackenzie), vol. i., p 188.

The first sal-ammoniac factory in Germany was that of the brothers Gravenhorst at Brunswick, founded in 1759. In Scotland it seems to have been first manufactured about 1750.

The present manufacture of ammonium chloride is carried on in various ways—either by direct saturation of gas-liquor or similar ammoniacal liquids (*e.g.*, from the manufacture of bone-charcoal, or from putrefying urine), or by decomposing ammonium sulphate with sodium chloride, or by passing ammonia vapour into hydrochloric acid.

At some English works sal-ammoniac is still made by *direct saturation of gas-liquor with hydrochloric acid*, mechanically agitated. The escaping noxious gases are conveyed into the boiler-fire and burned. The faintly acid solution is left to settle; in 3 or 4 days the tar has separated out at the bottom of the vessel. Sometimes it is necessary to pass the liquid through canvas filters. The solution of ammonium chloride, still dark brown, is evaporated by direct fire in iron pans, and is always kept neutral or faintly alkaline by means of a little lime, chalk, or ammoniacal liquor. During the evaporation tarry oils are again separated, and are skimmed off along with a little ferric oxide. The vapours ought to be condensed, as they cause a considerable nuisance. When the liquor has attained the required strength, it is run into tubs 8 ft. wide and 2½ ft. deep, where the crystallization is finished in 8 or 10 days. Every 6 or 8 hours it is stirred up in order to get small crystals, which are better for subliming. Finally the mother-liquor is run off by a plug-hole in the bottom, which is best made to slope to one side.

More rational is the plan followed at a French works (by the Compagnie Lesage), where the concentrated solution of ammonium carbonate and sulphide, obtained by one of the above-described apparatus (*e.g.*, Mallet's or Grüneberg's), is mixed with hydrochloric acid in a vessel lined with lead and provided with a pipe for carrying away the vapours, in such manner that both liquids run in at the same time and that a nearly neutral but faintly acid liquid is formed. Towards the end of the operation the temperature rises considerably, and there is much more danger of ammonia being carried away by the vapours, which must, of course, be dealt with in the ordinary manner to destroy the hydrogen sulphide. When the vessel is

full the supply is stopped, and the liquor is concentrated by a steam-coil up to the crystallizing point. The crystallization takes place in vessels lined with lead, and the crystals turn out quite white, if made from sewage. As very large crystals are not liked in trade, the contents of the crystallizers are stirred up two or three times a day. Naturally the size of the crystals also depends to a great extent on the concentration of the solution. When a solution of ammonium chloride is boiled down in iron vessels, as is sometimes done (especially in England) in order to allow of direct firing and to economize fuel, the liquid must always be kept alkaline, and the loss of ammonia occurring during the evaporation by the dissociation of a little ammonium chloride must always be made up. If the liquid once becomes acid, it quickly dissolves iron in the form of ferro-ammonium chloride, which is not decomposed by an excess of ammonia. Evaporating in lead is dearer, but much safer if any contamination with iron is to be avoided. Even metal cocks must be dispensed with, and must be replaced by indiarubber tubing and pinchcocks.

R. W. Hilgenstock (*Amer. Gas Light J.*, 1906, pp. 849 *et seq.*) treats weak liquor in the usual manner first by steam, then by lime, and absorbs the gases in water to yield a strong, pure solution of ammonia. This is run into neutralizing tanks, made of wood with a lining of hard-burned clinkers, laid in sulphur and glass dust, with two inlet pipes (for concentrated ammoniacal liquor and hydrochloric acid) reaching nearly down to the bottom, made of hard rubber, and a paddle for mixing the liquids. A wooden stack with a steam jet draws off the noxious vapours into the chimney stack or into a sulphur recovery apparatus. The inlet valves are regulated in such manner that the solution is always acid; but when the tank is almost full, the acid valve is closed and more ammonia liquor is run in until a sample, tested with methyl-orange, shows a clear "wine-yellow" colour. The liquor is now drawn off by means of a rubber hose into a wooden tank, where it is mixed with the mother-liquor from the crystallizing tanks, being always kept slightly alkaline, to avoid action on the pumps and coils in the concentrating tanks. These are made of wood, lined with hard-burned clinkers laid in best Portland cement, with a leaden or cast-iron steam-coil, with a cover and elbow

pipe, leading to a scrubber for removing the smelling gases. The evaporation is continued until a white skin is formed on the top. The liquor is then run into the filter-tanks, made of wood, with a false wooden bottom, on which boneblack of different sizes is packed, with a filter cloth on the top, and a small steam-coil to prevent crystallization. The filtered liquor runs into wooden crystallizing tanks, with wooden sticks to which the crystals adhere. The crystals are partially dried in a centrifugal extractor and afterwards (with continuous turning over) on a drying table, consisting of glazed terra-cotta tiles on small brick piers, heated by exhaust steam from the coals in the concentrating-pans.

Manufacture of Ammonium Chloride from the Sulphate.— For this purpose a concentrated solution of the latter is mixed with an equivalent quantity of common salt, and the whole is well agitated and boiled down, during which process monohydrated sodium sulphate is precipitated and ammonium chloride remains in solution:

$$(NH_4)_2SO_4 + 2NaCl = Na_2SO_4 + 2NH_4Cl.$$

The sodium sulphate is fished out with perforated spades and drained on copper plates, the liquor always running back into the pan. The salt is washed with a little water. The evaporation is continued until no more coarse crystals fall down, and the liquid begins to be covered with an opalescent pellicle of salt, which shows that the sodium sulphate is nearly all removed. The liquid is now allowed to cool in leaden vessels; and the crystallizing ammonium chloride is first washed with a solution of the pure salt, then with pure water.

Naumann (B. P. 654, of 1908; Fr. P. 378445, of 1907; Ger. P. 196260), instead of employing molecular proportions of ammonium sulphate and sodium chloride, uses an excess of the latter; in this case, on cooling, the ammonium chloride crystallizes out free from sulphate. The hot final solution should contain less than 75 parts of NH_4Cl to every 100 parts of water. Example: Dissolve 80 parts ammonium sulphate in 100 water at 70° C. or above, add 15 sodium chloride with agitation, digest for an hour or two, decant the liquor from any residue, and set to cool, when NH_4Cl, free from sulphate, will be separated. To the mother-liquor add ammonium

sulphate and repeat the process with further addition of sodium chloride.

Th. Schmidtborn (Amer. P. 330155) decomposes ammonium sulphate and *potassium chloride* into potassium sulphate and ammonium chloride. He describes his process as follows:[1]— In a lead-lined tub, with false bottom and agitating-gear, $2\frac{1}{2}$ tons ammonium sulphate are dissolved in water or in the washings of potassium sulphate up to sp. gr. = 71° Tw. The liquor is heated to boiling, and the exactly equivalent quantity of potassium chloride is put in, with constant agitation. The boiling is continued for another 10 minutes; the liquor is allowed to settle for half an hour, and is then run off. The potassium sulphate for the most part remains behind on the false bottom, and can be freed from ammonium salts down to $\frac{1}{2}$ per cent. by washing. Thus 70 per cent. of the total potassium sulphate are recovered. The washings are used for making a fresh solution of ammonium sulphate. The hot liquor on cooling deposits more potassium sulphate, and a further quantity on concentration. By a second concentration and cooling down, a mixture of salts is obtained in two distinct layers: the upper three-fifths consisting of 94 per cent. ammonium chloride, with 6 per cent. potassium and sodium sulphate and sodium chloride; the lower two-fifths consisting of 78 per cent. ammonium chloride and 22 per cent. potassium sulphate. The upper layer can be converted into 98 or 99 per cent. ammonium chloride by mere washing; the lower by recrystallizing. For the latter object, the salt is suspended in perforated trays in boiling liquor, which dissolves out the ammonium chloride within a few minutes; the crystalline potassium sulphate remains behind on the trays and is lifted out in them. On cooling, the ammonium chloride crystallizes out, and is drained by means of a centrifugal machine, as well as the potassium sulphate. The former is also stove-dried; the latter is sold as it is. This process, which has been actually carried out by the inventor, is claimed by him as an improvement upon the analogous process with sodium chloride, because there is no partial redecomposition on the liquors cooling down. He also claims that the value of the potassium chloride is more than covered by that of the sulphate obtained.

[1] *Chem Zeit.*, 1886, p. 1499.

Other Processes for the Manufacture of Ammonium Chloride.

Kuentz has proposed to make sal-ammoniac by direct distillation of ammoniacal liquor into an acid solution of phosphate of lime, produced by dissolving native phosphate of lime in hydrochloric acid:

$$Ca_3(PO_4)_2 + 4HCl = CaH_4(PO_4)_2 + 2CaCl_2.$$

The reaction taking place with the ammonium carbonate distilled into the solution, or added in the shape of concentrated liquor, produces a precipitate of dicalcium phosphate and calcium carbonate, which is a much more valuable manure than the native phosphate, and a solution of ammonium chloride. The object of this process is to save the acid required for making superphosphate or "precipitated phosphate," as this acid is altogether turned into sal-ammoniac; but the process does not seem to have found a practical application. Its theoretical equation would be:—

$$CaH_4(PO_4)_2 + 2CaCl_2 + 2(NH_4)_2CO_3 = 2CaHPO_4 + CaCO_3 + 4NH_4Cl + CO_2 + H_2O.$$

Another process proposed by Kuentz consists in treating the raw gas-liquor with impure ferrous chloride, made from pyritous schist and common salt. There is thus obtained a solution of ammonium chloride and a precipitate of ferrous carbonate and oxide mixed with a little sulphide, which is an excellent material for purifying coal-gas. In this process no noxious gases are given off.

Another process is one in which "concentrated gas-liquor" (p. 975) is mixed with a solution of calcium chloride (which is a waste-product of many chemical operations and without any value) till all the lime is precipitated; the mass, passed through a filter-press, yields cakes of calcium carbonate and a solution of ammonium chloride, which should be acidified with hydrochloric acid, to destroy any sulphide. The calcium carbonate carries down most of the impurities; so that even ammoniacal liquors from the destructive distillation of bones and other animal matters can be treated in this way for pure ammonium chloride.

Gentles (B. P. 2224, of 1878) distils the ammonium carbonate, etc., from gas-liquor into a crude solution of calcium chloride,

contained in a vessel with agitating-gear. The solution is separated from the precipitate, is acidified in order to precipitate any arsenic as trisulphide, and the clear filtrate is again made alkaline with ammonia, to precipitate any iron as oxide. These processes, founded on the application of calcium chloride, appear to deserve attention.

Dubose and Henzey (*J. Soc. Chem. Ind.*, 1890, p. 614) decompose gas-liquor by the exact proportion of a solution of calcium and ferric chloride, with formation of FeS and $CaCO_3$. The mixed liquids are allowed to stand for 12 hours, when the upper two-thirds can be drawn off clear. The precipitate is an excellent gas-purifier. The solution, about 7° Bé., is evaporated in small iron pans to 13° Bé.; the vapours pass into a chimney. The concentrated liquor is run into wooden coolers, where it remains a fortnight. During this time the upper crust of crystals is broken up every day, to obtain needle-shaped crystals. Cubical crystals are obtained by adding to the liquor 5 per cent. of a solution of ferric chloride (*cf.* Adler, *infra*). The crystals are drained and dried at 50° or 60°, or carefully roasted in a reverberatory furnace. A brownish-yellow colour (which seems to be preferred in France) is obtained by adding a little slaked lime (which evidently produces ferric hydrate from adhering ferric chloride). "Refined" product is obtained by stopping the concentration at 11° Bé., and precipitating the iron by ammonium sulphide and boiling down in enamelled cast-iron pans. Any cracks in the enamel should be mended by a mixture of cement, silicate of soda, and hydrofluosilicic acid. The concentrated liquor is allowed to crystallize in earthenware dishes.

The same authors describe the manufacture of ammonium chloride from ammonium sulphate by double decomposition with calcium chloride, or, preferably, ferrous chloride (obtained on pickling iron), allowing the ferrous sulphate to crystallize out, removing the iron from the mother-liquor as above, and obtaining the ammonium chloride from the last liquor.

A detailed description of the manufacture of ammonium chloride from *waste-liquors of ammonia-soda works* is given by Adler.[1] After driving off the ammonia (both "volatile" and "fixed") in the ordinary steam-column, the residual liquor is

[1] *Z. angew. Chem.*, 1899, pp. 201 and 226.

clarified by subsidence, and the clear liquor freed from lime by treatment with carbonic acid. After filtration, the liquor is concentrated in an ordinary salt-pan to exactly 20° Bé., up to which point no sodium chloride falls out. The concentration is continued in a smaller pan, fishing out the sodium chloride at regular intervals. At 32° Bé. most salt is removed, but an almost quantitative removal requires concentration to 40° Bé. in winter, or 44° Bé. in summer. The cooled and clarified liquor then contains only about 3 per cent. NaCl; 1 litre of winter liquor contains about 680 g., of summer liquor 580 to 600 g. calcium chloride.—The second liquor required, viz., a solution of ammonium carbonate, is obtained by washing the gas given off on calcining the sodium bicarbonate; it contains at least 2 per cent. of ammonium carbonate, with a little free NH_3, etc.

These liquors are now mixed in the cold, after having diluted the $CaCl_2$ solution to 10° or 20° Bé., in order to obtain the $CaCO_3$ in the proper shape, leaving a small excess (3 to 5 per cent.) of $CaCl_2$. The vessel in which this is effected is cylindrical, with a conical bottom, provided with stirring-gear and an outlet-cock at the bottom. The calcium carbonate should be quickly and completely removed when formed, to prevent the conversion of the rhombic arragonite crystals into rhombohedric calcite crystals. The decomposition is finished when a filtered sample yields no precipitate with calcium chloride. If free NH_3 is present, the solution formed must be treated with the exactly corresponding quantity of hydrochloric acid. The separation of the precipitated calcium carbonate from the ammonium-chloride solution is best effected by a wooden filter-press, to prevent contamination with iron. After pressing, the residue is first washed with washings from a previous operation, then with pure water, and then treated with a current of air; the cakes of calcium carbonate leave the press with 50 per cent. moisture, and can be dried in various ways.

The boiling-down of the ammonium-chloride solution is best performed in lead-lined pans; the small quantity of lead passing into the product is immaterial for technical purposes. The heating is done by means of leaden steam-coils, up to the time when a pellicle of salt appears on the

surface. The liquor is now run off into lead-lined iron or wooden coolers, which may be shallow or deep. For some purposes small crystals are preferred, in which case the liquor is stirred from time to time. The mother-liquor remaining after crystallization is evaporated separately and is eventually removed, when too impure.

The crystals formed in the first liquor are at once marketable, after draining and drying, which is best done on wooden frames covered with jute sacking, in steam-heated stoves. The crystals formed in mother-liquors must be freed from adhering calcium chloride by recrystallization.

Specially fine crystals, according to Adler, can be obtained as follows:—Mother-liquor, containing more $CaCl_2$ than the first liquor, is boiled down up to the formation of a salt pellicle, then mixed with an equal volume of first liquor and at once run into the coolers, during which time it is mixed with a similar solution of cupric sulphate (0·01 g. to 1 litre). After 24 hours the first octohedric crystals are formed at the sides and the bottom of the vessels, which increase and are of remarkable transparency and hardness, not obtainable without the cupric sulphate. Sometimes crystals 4 inches in length are thus obtained; usually they are 2 inches or a little more.

The Solvay Processes Company (U.S. P. 805581) obtain ammonium chloride by the simultaneous action of dry NH_3 and CO_2 on to a concentrated (1·38 sp. gr.) hot solution of calcium chloride. The $CaCO_3$ is removed by settling out, and the solution on cooling yields the ammonium chloride.

A very peculiar process is that of Th. Heskin (B. P. 2491, of 1884). He decomposes sodium borate by sulphuretted hydrogen, dissolves the separated boric acid in strong liquor ammoniæ, and decomposes the ammonium borate with common salt, whereby sodium borate is regenerated.

Drovieusat (B. P. 20613, of 1907) makes ammonium chloride by adding sea-salt to a saturated solution of ammonium sulphite at 40° C., and raising the temperature to 95°. Sodium sulphite is deposited and separated hot from the mother solution, which, on cooling to 40°, deposited ammonium chloride. The mother solution now remaining is again charged with sulphite of ammonium and sea-salt, heated to 95°, and treated as before.

French (U.S. P. 882460) drenches carbonized coal with strong brine and burns it in a current of air containing at least 10 per cent. steam, whereby ammonium chloride is said to be produced.

Properties of Crude Ammonium Chloride.

The *crude ammonium chloride* is coloured more or less dark by tarry matters, and contains other impurities, especially ammonium sulphate and thiosulphate, as well as moisture. It is dried in layers 4 inches thick, on metal plates heated by the waste heat of the subliming-pans, but not to the point of volatilization. Here the water and free acid are volatilized, and the tarry matters are mostly carbonized. The roasted salt is of a grey-white colour, and should be conveyed as quickly as possible into the subliming-pots, lest it again attracts moisture. If the crude salt has been made by direct saturation of gas-liquor with hydrochloric acid (a process which ought to be given up as quite irrational, and as causing a great nuisance; *cf.* pp. 964 and 1112), in drying or roasting it produces a very bad smell, which is absent when the salt has been made from distilled ammonia.

Purification of Ammonium Chloride by Sublimation.

Sometimes the subliming is done in long rows of earthenware pots or glass carboys. This is the process used in Egypt and other Oriental countries, and it is still exclusively practised in France, since the buyers there demand the small cakes obtained by this process. But this is expensive, on account of the labour and the loss of the vessel in each operation. Hence in England iron pots are exclusively used, either cast in one piece or composed of several pieces, 3 to 9 feet in diameter. Large pots are far preferable to small ones, as the latter require nearly as much fuel, labour, and time for working off as the former. They are lined with firebricks, and are heated by a fire from below and by annular flues all round. Their bottoms are, by preference, concave, so as to present a larger heating-surface. The pots are covered with concave plates, provided in three places with rings for chains, by means of which they can be lifted off by a travelling crane, etc. The covers are perforated in the centre; the aperture is closed by an iron rod, which

is removed from time to time to allow the permanent gases to escape. They are covered with some non-conductor of heat. Pots 3 feet wide hold 10 cwt., those 5 feet wide 15 to 18 cwt., and those 9 feet wide 2 to 2½ tons of salt.

The operation must be exactly regulated. At first a brisk fire is made; but this is slackened directly the sublimation commences, since at a very high temperature too much empyreumatic matter is evolved and disturbs the solidification of the salt. At too low a temperature the sublimate is loose and not transparent, which makes it difficult to sell. The cover ought to be at such a heat that a drop of water begins to boil on it and evaporates quickly. The first layer adhering to the cover is always brownish, probably because a little water always remains in the roasted salt, which condenses on the cover and loosens ferric oxide. Later on a coloration may be caused by ferric chloride. The sublimation may last from 5 to 9 days, but is usually interrupted after a week by lifting the cover, the fire having been damped up some time before. The sublimation is not driven to the last; for then the temperature would rise too high, the carbonaceous impurities would be decomposed, and the vapours would injure the appearance of the sal-ammoniac. On the cover is found a layer from 2½ to 4 inches thick, which is knocked off. The above-mentioned brown stratum is hacked off with a hatchet or planed off.

The French subliming-process is illustrated by Figs. 302 and 303. It is carried on in earthenware pots, P, about 18 inches high and 12 to 14 inches wide, of which about 20 are placed, in two rows, in a galley-furnace heated at one end. The pots stand on an arch, perforated by pigeon-holes, *o o*; they are supported at two-thirds of their height by the cast-iron plate F, on which a layer of sand is spread quite to the top of the pots. After being charged with dry crystallized ammonium chloride, which is sometimes mixed with about 20 or 30 per cent. of animal charcoal, they are placed in the furnace, covered up with sand, and at first gently heated to avoid cracking. The moisture still present escapes through the openings *s s*, and soon the thick white vapours of sal-ammoniac appear, whereupon an ordinary flower-pot, *p*, is put on as a cover. The sublimate collects partly in the upper portion of the pots P, and partly in the flower-pots, *p*. The openings *s s* gradually get stopped up;

and towards the end of the operation, when the fire has to be increased so as to produce the dense and translucent appearance of the product required in commerce, there is a certain pressure

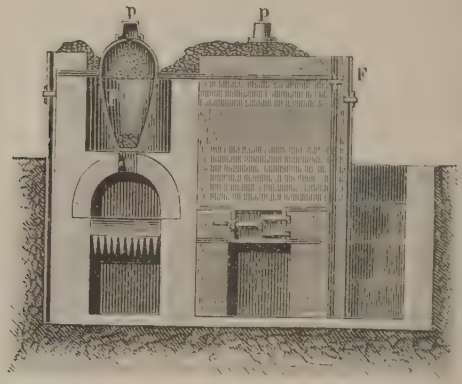


FIG. 302.

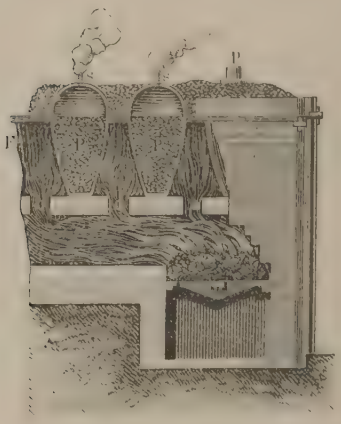


FIG. 303.

in the apparatus. In order to obtain sufficiently large cakes, the pots must be charged several times over again. For this purpose the openings are cleared again and the operation is repeated. After two or three charges the cakes are large

enough; the pots are now taken out when sufficiently cool, and are broken in order to get out the sublimate. The whole takes about 2 days. In some places, in lieu of earthenware pots, glass flasks or carboys are used on account of cheapness. These are usually about 1 foot wide and 2 feet high, and hold 20 lb. of the mixture of dry ammonium chloride and charcoal. They are placed in a double row of 8 or 10 each in metal pots, heated by a galley-furnace. The pots serve as sand-baths, and the flasks are placed about two-thirds in the pot; the last third projects outside, but is covered with a layer of sand up to the neck, which is covered with a piece of sheet-lead. When this appears covered with a glassy sublimate of sal-ammoniac, the projecting part of the flask is cleared of sand, and care is taken lest the lead should adhere too fast to the flask, by knocking on its lower side from time to time. When the sublimate is glass-like, and the lead plate, on knocking from below, is no longer lifted up by the vapours evolved, it is left quietly on the top; but the upper opening must never be allowed to become entirely stopped up, which is prevented by boring in with a pointed iron. The operation lasts from 12 to 16 hours. The lead covers are then taken away, and are replaced by corks or by pieces of cotton-wool, and the whole is allowed to cool down slowly. During the cooling the sal-ammoniac expands and cracks the glass. The cake, freed from glass, is scraped with a knife, to remove all dirt, and is packed in the shape of loaves; it is crystalline and perfectly white.

The French sal-ammoniac being thus made in earthenware or glass vessels, is purer than the English article sublimed in iron pots. The destruction of the subliming-vessels at each operation makes it a costly product; but it might no doubt be made much more cheaply in stoneware vessels consisting of two parts, which would stand a number of operations.

Some consumers, especially in France, require the sublimed sal-ammoniac to look as grey and dirty as that formerly made in Egypt from camels' dung; this is effected by adding some greasy matter to the salt before sublimation, or in small portions during the operation, so that some soot gets mixed with the sal-ammoniac. Otherwise it ought to be white, transparent, of fibrous texture, and firm, not porous and light. Sometimes a few per cent. of monocalcium phosphate or of ammonium

phosphate are mixed with the salt before subliming, to retain any iron. This is also recommended by Adler (*loc. cit.*), who adds to the crude ammonium chloride 20 or 25 per cent. commercial superphosphate, and heats without putting on the lid, until white vapours begin to appear. The operation proceeds all the better the slower the heating. The lid should be milk-warm only.

Calvert proposed, in order to make the sublimation cheaper and continuous, and to obtain the product in a shape more convenient for use, to dry the muriate of ammonia very briskly and distil it from a set of fireclay retorts, alternately charged into large brick chambers covered with a smooth coating of cement inside, on which the sal-ammoniac would be deposited as a fine powder. This process, which looks very rational indeed, was tried on the large scale, but was given up, and is not in use anywhere at present, probably because the consumers insist upon the fibrous transparent texture of the product, which they believe (although erroneously) to guarantee its purity. Calvert also tried adding animal charcoal and phosphates before subliming; but his sal-ammoniac was never free from iron.

Commercial sal-ammoniac appears in the form of cakes or disks, weighing from 10 to 40 lb., sometimes as much as 1 cwt., white, translucent, of fat-like brilliancy, hard and resonant. They are formed of parallel layers of a fibrous texture.

Pure Crystallized Salt (Muriate of Ammonia).

Besides sublimed sal-ammoniac, the crystallized salt, usually called *muriate of ammonia*, is also found in the trade at a much lower price. To obtain this, the crude salt is once or several times recrystallized, and the solution each time filtered through animal charcoal. It is also made into the shape of loaves, the crystals being stirred up to a paste with a hot saturated solution, and the whole being allowed to solidify in conical sugar-moulds of glazed earthenware. The opening at the bottom is at first closed by a plug, which is removed after a few days; the mother-liquor then drains off. The loaves are taken out by inverting the moulds, and are dried in a stove; they turn nearly as hard as loaf-sugar. Most ammonium chloride, however, is sold in the form of sublimed sal-ammoniac.

The consumers insist upon having it in this shape, although it generally costs twice as much as the crystallized salt, and is no better. An attempt made by the French Company Lesage to replace it by strongly compressed cakes of crystallized salts, in disks of 4 inches diameter and 1 inch thick, failed for want of support from the buyers. Hempel (*Berl. Ber.*, xxi., p. 897) mentions that this was done by strong hydraulic pressure at temperatures between 50° and 100° C.

Further Purification of Ammonium Chloride.

For some purposes it should be entirely *free from iron*. Formerly it was believed that this was always the case with colourless sal-ammoniac; but Wurtz has shown that only ferric chloride is indicated in sal-ammoniac by the ordinary reagents, while ferrous chloride cannot be discovered either by the colour or by the ordinary reagents. The ferrous can be formed from the ferric chloride by the reducing action of sal-ammoniac itself, thus:—

$$3Fe_2Cl_6 + 2NH_4Cl = 6FeCl_2 + 8HCl + 2N.$$

In order to make a product entirely free from iron, a little chlorine gas is passed through the boiling-hot solution of ammonium chloride (an excess of chlorine would produce that fearfully explosive substance, nitrogen chloride); ammonia is added, which precipitates all the iron now present as peroxide; the liquid is quickly filtered and crystallized. A salt free from iron is said to be obtained also by adding a little calcium phosphate before sublimation (see preceding page).

The preparation of chemically pure ammonium chloride for the purpose of atomic-weight determinations is described by Hinrichsen in *Z. anorg. Chem.*, 1908, lviii., p. 59, and *Z. angew. Chem*, 1908, p. 1081.

Uses of Ammonium Chloride.

Ammonium chloride is used in pharmacy, in soldering, in galvanizing iron; for making the ordinary rust cement from 100 parts iron filings, 4 brimstone, and 1 sal-ammoniac; in calico printing, in the manufacture of colours (for the last-named purpose it is mostly required to be free from iron; *vide supra*).

A not inconsiderable quantity of crystallized ammonium

chloride is used for feeding the Leclanché cells generally employed in telegraph-offices, etc. For this purpose it should be free from lead, which is very injurious for the working of the cells, and should therefore be freed from metals by ammonium sulphide.

Enormous quantities of ammonium chloride are produced as an intermediate product in the manufacture of ammonia-soda; but these are always reconverted into free ammonia, to be used over again, and we must refer to the treatment of this subject in Lunge's *Sulphuric Acid and Alkali*, vol. iii.

Whitehouse (B. P. 15140, of 1907) prepares ammonia and chlorine or hydrochloric acid from ammonium chloride, by heating it to 300° C. in mixture with the oxides or oxychlorides of cerium, thorium, didymium, lanthanum, or yttrium. NH_3 and water are expelled. The resulting chlorides of the above metals are heated in a current of air or steam, whereby Cl or HCl are evolved, and the oxides of the metals remain behind.

Ammonium Fluoride, NH_4F.

This salt forms hexagonal scales or prisms, of sharp, salty taste, deliquescent in moist air. It is obtained by passing hydrogen fluoride into liquor ammoniæ. In the moist state it decomposes silicates at ordinary temperatures, in the dry state at higher temperatures, and is therefore employed for etching glass. On evaporating its solution at 40 an acid salt, NH_4F,HF, is formed which crystallizes in colourless prisms, but is a little deliquescent. It must be kept in bottles of lead or guttapercha.

For manufacturing it on the large scale, Mills (G. P. 94849) mixes finely ground ammonium sulphate with ground fluor-spar, and heats the mixture gradually above 350° C. in a cast-iron pan, lined with a thin layer of gypsum, and provided with a concave lead lid, cooled on the outside by water. The ammonium fluoride, formed by the reaction

$$(NH_4)_2SO_4 + CaF_2 = CaSO_4 + 2NH_4F,$$

sublimes with a little sulphate, and is condensed on the inside of the lid.

This salt is employed for etching glass, for decomposing certain minerals containing rare earths serving for incandescent

mantles, and for preparing certain fluorides (especially of antimony) employed in the dyeing industry.

Ammonium Ferrocyanide.

Grossmann (B. P. 19988, 1907) obtains this by agitating gas-liquor with an excess of iron sulphide, in the presence of considerable quantities of ammonium sulphide, access of air being avoided. The necessary quantity of FeS is ascertained by a laboratory experiment. The clear liquor is distilled for NH_3 in the usual manner, and in the residual liquor the ferrocyanide is precipitated after acidification by adding iron compounds (*cf.* his B. P. 20387, of 1905, *supra*, p. 1052). He discusses this in detail in *J. Soc. Chem. Ind.*, 1908, pp. 393 *et seq.*

Ammonium Sulphocyanide (Thiocyanate).

This salt has lately come into use in dyeing and calico-printing, both directly and as a starting-point for the preparation of other sulphocyanides;[1] hence it is manufactured on an industrial scale. It can be prepared by synthetical methods,[2] but we first mention its recovery from ammoniacal gas-liquor. It remains behind when the volatile ammonium compounds are expelled by steam. From this residue cuprous sulphocyanide can be obtained by adding a mixed solution of the sulphates of iron and copper. This was done by P. Spence,[3] who, after washing the precipitate, decomposed it by ammonium sulphide into copper sulphide and pure ammonium sulphocyanide. Similar to this, but hardly preferable, is the process of Storck and Strobel,[4] who saturate gas-liquor with hydrochloric acid and precipitate the sulphocyanide by a mixture of cupric chloride and sodium bisulphite. The precipitate of cuprous sulphocyanide is washed, boiled with a solution of barium hydrate, and the barium sulphocyanide allowed to crystallize.

[1] *Cf.* Storck and Strobel, *Dingl. polyt. J.*, ccxxxv., p. 156; Glenck, *ibid.*, ccxli., p. 399.

[2] *Cf.* especially Tscherniak and Günzburg's Ger. P. 399; *Dingl. polyt. J.*, ccxxxii., p. 80. A new patent was taken out by them in 1881; and an exact description of their latest plant is given in the *Bull. Soc. Ind. Mulhouse*, 1882, p. 77. Their factory has since ceased working.

[3] *Chem. News*, xviii, p. 119.

[4] *Dingl. polyt. J.*, ccxxxv., p. 156.

Phipson[1] mentions another process known in London, but does not say in what it consists. The thiocyanate is especially easy to recover when applying the Claus process for purifying gas; it is found as a sodium salt in the residual liquor from distilling off the ammonia by means of caustic soda, and is recovered by evaporation, or precipitation, in the state of cuprous thiocyanate. The amount of sodium thiocyanate is 2·3 lb. per ton of coal.

The British Cyanides Co. and K. M. Chance (B. P. 6218, of 1908) wash coal-gas with a liquor containing alkaline polysulphide, which reacts with some of the cyanogen and forms thiocyanate and H_2S. The latter is passed, together with the gas, into a second washer, containing ammoniacal gas-liquor, in which free sulphur is kept in mechanical suspension; NH_3, H_2S, and S combine to form ammonium polysulphide, which removes the remainder of the cyanogen from the gas in the form of thiocyanate.

Crowther (B. P. 11964, of 1893) precipitates by CO_2 the lime from spent gas-liquor, and after settling treats the clear liquid with a paste of cuprous oxide, after which the mixture is slightly acidulated with HCl, and the cuprous sulphocyanide filtered off. By treating it with carbonates or hydroxides of alkalis the respective salts are obtained and the cuprous oxide is recovered.

We have seen before (p. 887) that ammonium sulphocyanide occurs in large quantities in the ammonium salts made by lixiviating *spent oxide* from the purifiers of gas-works. It should be possible to separate the sulphate from the sulphocyanide by fractional crystallization. As a rule, 10 to 30 per cent. of the latter salt is present in the total ammonium salts (*cf.* Gasch, *Chem. Zeit.*, 1886, p. 214).

According to a patent of Marasse (Ger. P. 28137) the spent oxide, which after lixiviation still contains a great deal of sulphocyanide, is heated in a closed vessel, with an excess of lime and water, to a temperature exceeding 100° C. The products of this treatment are ferrous sulphate and calcium sulphocyanide, the latter of which is recovered by lixiviation, and serves for preparing other sulphocyanides. (*Cf.* also Wolfrum's process, p. 1058.)

Esop[2] discusses at length the treatment of spent oxide of iron. This contains the ammonium sulphocyanide irregularly

[1] *Chem. News*, xviii., p. 131. [2] *Chem. Ind.*, 1892, p. 6.

dispersed in microscopical crystals. In cool places, protected from the weather, it keeps for some time, but at a somewhat higher temperature the sulphocyanide rapidly decomposes. This may take place on keeping the mass in deep layers in the damp state, which may even lead to the sulphur taking fire. The sulphocyanide in this case is replaced by ferrocyanide and sulphate. In order to extract the sulphocyanide from the spent oxide, this must be finely ground and methodically lixiviated, preferably with the aid of filter-presses, by which liquors of sp. gr. 1·028 to 1·113 can be obtained. They are of yellow, green, or blue colour, but this vanishes later on during the further treatment. Weak liquors (1·070 to 1·085) are not evaporated, but treated with cuprous oxide; those containing less than 2·3 g. sulphocyanide per litre are not worth treating at all. Stronger liquors are evaporated in vessels of nickel, lead, tin, aluminium, or preferably of enamelled iron. By evaporating to 22° or 27° Bé. and cooling, crystals of ammonium-sodium sulphate and ammonium sulphocyanide are obtained; from the mother-liquor by further evaporation a purer sulphocyanide is obtained, which on crystallization is of light yellow colour and contains 80 or 90 per cent. sulphocyanide. A purer article is made from this by precipitating both iron and sulphate by means of barium sulphide and recrystallizing. *Chemically pure* ammonium sulphocyanide is prepared by first converting it into the barium salt by means of caustic baryta, or by the action of barium sulphide on cuprous sulphocyanide. The former is done in closed vessels at 0·2 to 0·4 atmospheres' pressure and 80° to 90° C., driving off the NH_3 by steam as quickly as possible. The second process causes no loss of sulphocyanide and saves any evaporation. The raw gas-liquor or extract from spent oxide is treated with cupric sulphate and sulphurous acid at ordinary temperatures, or at most at 40° or 50° C. The heavy light-grey precipitate of cuprous sulphocyanide, containing traces of sulphide, etc., is washed ten times by decantation and is decomposed by a solution of barium sulphide, of 15° Bé., in excess, which acts perfectly; whereas Crowther's proposal of employing alkaline hydrates or carbonates (p. 1128) yields a very imperfect result. It is preferable to employ at first an insufficient quantity of barium sulphide, and to decompose the remainder by an excess of this salt, reserving this liquor for the

next operation. The colouring-matter is carried down with the copper sulphide. The clear solution of barium sulphocyanide is boiled down to 57° or 60° Bé., and yields very good crystals. The copper sulphide, after pressing and drying, can be roasted in pyrites-burners, and the remaining oxide used over again as before. The barium sulphocyanide, by treating with ammonium sulphate, yields perfectly pure ammonium sulphocyanide.

The synthetical preparation of sulphocyanides is performed by the action of ammonia and carbon disulphide at a temperature of 120° and 130° and at a pressure of 15 atmospheres (*cf.* Tscherniak and Günzburg, p. 1127). This subject belongs to the cyanides, and we therefore mention quite briefly the following patents: Hood and Salamon (Ger. P. 72644), who add an oxidizing agent like manganese or ferric oxide, in order to convert the H_2S into S; British Cyanides Co., Ltd. (B. P. 14154, of 1894; Ger. Ps. 81116 and 85492), who dispense with the oxidizing agent but add a base, like lime; Goerlich and Wichmann (Ger. Ps. 87135 and 89811), who heat ammonium nitrite with carbon disulphide and sulphuretted hydrogen to 150°; Goldberg and Siepermann (Ger. Ps. 83454 and 87813), who add sulphite or thiosulphate, also with the idea of avoiding the formation of H_2S and forming S.

Ammonium Carbonate.

Commercial carbonate of ammonia (sal-volatile), as has been explained on p. 954, is really a mixture or a compound of ammonium bicarbonate and carbamate, and as such is always formed on subliming. Hence the name frequently used for it, "ammonium sesquicarbonate," is incorrect, although the salt actually often contains four molecules of NH_3 to three of CO_2.

In 1870 Divers (*cf.* p. 952) found the article then manufactured to contain more ammonia, in the proportion of three molecules of NH_3 to two of CO_2; but in 1886 Hanekop and Reissmann, on the contrary, found an article consisting of one molecule of NH_3 to one of CO_2 (p. 953), that is, really, ammonium bicarbonate; and Topf, in 1887, confirmed this with several samples of the commercial article analyzed by him (*Z. anal. Chem.*, xxvi., p. 158). Evidently different mixtures or compounds of ammonium salts have come into the trade, at different times, and probably even at the same time, under the name of "ammonium carbonate."

Ammonium carbonate is formed in the destructive distillation of animal matters, and is often found as a solid deposit in the refrigerator, if the substances employed have been dry. This deposit, which forms brown crusts, was formerly known as "salts of hartshorn," and was always accompanied by a watery liquid, a saturated solution of ammonium carbonate, known as "spirits of hartshorn." Both are very much contaminated with tarry products, and cannot be purified by one redistillation, but only by a third distillation with boneblack. This manufacture is rarely carried out now.

Commercial ammonium carbonate is now usually made by mixing ammonium sulphate with calcium carbonate and subliming. Calcium sulphate remains behind in the retort; and the mixture of ammonia, carbon dioxide, and aqueous vapour (which must not be absent) condenses on cooling to solid carbonate of ammonia. A mixture of 1 part ammonium sulphate with $1\frac{1}{2}$ or 2 parts of finely ground chalk, sometimes with a little charcoal powder, is heated in horizontal cylindrical cast-iron retorts, several of which are usually heated by the same fire, like gas-retorts. At first the heat should not be great; but at last it must attain redness.

The vapours are conveyed by a wide pipe into lead chambers, usually two or more in succession, provided with a door for the removal of the salt. From the last chamber the vapours pass through sulphuric acid, preferably trickling down in a small leaden coke-tower. In the chambers the condensation is effected solely by air-cooling; but they may be surrounded by a jacket to cool them by water. Several operations are performed in succession, till a sufficiently thick crust has formed, which is loosened by blows outside with a hammer, and is completely broken off after opening the doors. This crust must not be allowed to become too thick, as otherwise the air-cooling will be too imperfect and the salt will become too hard and difficult to detach.

A convenient plan (Fig. 304) is to employ five retorts, *a*, 18 inches in diameter and 7 feet long, heated by one fire, *b*, with two condensing-chambers, B, C, both 8 or 10 feet long and wide and 7 feet high. The retorts may be charged alternately every 8 hours. Each retort-cover has an aperture for a rake, to stir up the mass during the operation. The

process in such an apparatus can go on for a fortnight before the chambers need be emptied, when the men adopt the precaution of tying sponges drenched in vinegar over their mouths and noses. During the work care must be taken lest the connecting-pipes, *c*, *d*, between the retorts and chambers get choked up.

In the bottom of the condensing-chambers there is a pipe for running off a little solution of ammonium carbonate, formed from the excess of moisture; here also a little steam escapes.

The product of this first operation is still very impure, at least if crude ammonium sulphate has been employed; it is then discoloured by tarry matters, and is sometimes sold as

FIG. 304.

"ammonium carbonicum pyro-oleosum." It also mostly contains a little chalk or calcium sulphate carried over. According to Divers (p. 952), whose observations have been confirmed by myself, this product has not the composition of commercial ammonium carbonate, no ammonia escaping during the distillation, but is normal ammonium carbonate, $(NH_4)_2CO_3$, or, more probably, ammonium carbamate, $(NH_4)CO_2(NH_2)$. With a leaky and warm receiver, however, acid carbonate is formed, and the latter, that is, the commercial salt, is always produced in resubliming the first product.

This product, being too impure, is generally converted by resubliming into a white salt, forming fibrous transparent cakes 2 inches thick. This can be done, with hardly any expense, by

the waste heat of the retort-furnace, which travels underneath a row of iron pots covered with lead cylindrical caps. The crude salt is put into the pots, along with a little water (without which the pure salt would not be transparent). Sometimes the pans are not exposed to the direct fire, but are placed in a common water-bath, heated by the waste heat of the retort-fire. A temperature of 70° suffices for resubliming; and it is best not to exceed this, because the salt turns out finer and less is lost by volatilization. The lead caps into which the salt is to sublime are made by rolling a sheet of lead into the shape of a cylinder, about 12 inches wide and 2 feet 6 inches high, covering this at the top with a piece of sheet-lead, and pasting up the joints with paper. When the sublimation is finished, the lead is unrolled and the cake of salt can be taken out at once.

Another apparatus for resubliming[1] consists of an iron pan 2 feet 6 inches wide at the bottom and 2 feet at the top, 15 feet long, and 2 feet 6 inches high, in the cover of which there are eight 12-inch holes, on which are placed conical lead caps, 2 feet 6 inches high, kept in their shape by clamps or wedges. With these it is possible to work 14 days uninterruptedly. Then the clamps or wedges are loosened, and the mass is taken out; but it must be scraped off clean where it adheres to the lead. The salt is mostly packed in stone jars. Some liquid remains in the iron pan, most of which is left behind for the next operation.

The different qualities of white ammonium carbonate found in commerce seem to be obtained by heating more or less quickly, and by putting more or less water into the charges.

The usual process for making ammonium carbonate, as just described, does not appear to be quite rational. In the finished salt there is $1\frac{1}{2}$ times (or, in the salt analyzed by Divers, $1\frac{1}{4}$ times) as much carbon dioxide as in the neutral salt; but according to the conditions of the process there is only enough CO_2 for the latter. Hence a large quantity of ammonia must go away in the uncombined state. This might be remedied by passing carbon dioxide into the subliming-apparatus; even an excess of this would not interfere with the formation of the ordinary ammonium carbonate.

(This suggestion, which was put forth in the 1882 edition of

[1] Bell, *Chem. News*, xii., p. 303.

this work, has since been acted upon successfully by at least one manufacturer of carbonate of ammonia.)

Other Methods for manufacturing Ammonium Carbonate.

Kunheim & Co., of Berlin, manufacture this salt in the most direct manner, by bringing together the gaseous mixture from the distillation of gas-liquor with carbon dioxide in lead chambers, thus producing the commercial salt.

Seidler (Ger. P. 26633) distils crude gas-liquor over limestone or dolomite, whereby the fixed ammonium salts are decomposed, so that the distillate contains, besides ammonium carbonate, only a little sulphide. This is removed by treating the concentrated aqueous solution with CO_2, and the commercial salt is produced from the precipitated crude ammonium carbonate by sublimation.[1]

F. C. Glaser (B. P. 5761, of 1884) heats salts of ammonia with equivalent quantities of sodium carbonate, to which a small quantity of bicarbonate has been added. The reaction is said to take place in a more perfect manner.

F. C. Teed (*J. Soc. Chem. Ind.*, 1885, p. 709), from experiments on a small scale, makes a proposal similar to Seidler's, viz., running a solution of ammonium chloride slowly down a tower filled with small pieces of calcium carbonate, steam being blown up at the same time. Solid ammonium carbonate forms at the top.

Wächter (G. P. 34393) injects a spray of ammoniacal liquor, by means of a compressor, into a red-hot retort filled with calcium carbonate.

A method formerly employed by Kunheim & Co. consisted in subliming ammonium chloride with barium carbonate, to obtain barium chloride as a by-product.

Chatfield (B. Ps. 6151 and 6152, of 1888) decomposes ammonium sulphate by magnesia, passes the NH_3 into water and CO_2 into this solution; when it shows 20 Bé. it is distilled with a further addition of CO_2, the distillate freed from steam and the ammonium carbonate condensed.

H. R. Lewis (B. P. 14618, of 1895) passes waste gases from

[1] Details of the apparatus in *Dingl. polyt. J.*, cclii., p. 476, and *J. Soc. Chem. Ind.*, 1885, p. 112.

lime-kilns, blast-furnaces, etc., together with the gases from ammonia-stills, into condensers where crystalline ammonium carbonate is formed, the escaping NH_3 being condensed in a suitable manner. The carbonate is purified from sulphide by a current of air, or is washed and dried; or is converted into bicarbonate by CO_2 and moisture.

Raspe (Ger. Ps. 70977 and 83556) obtains ammonium carbonate directly from the products of dry distillation of coal, etc., by freeing them, before distillation, from sulphides and empyreuma by means of zinc carbonate and oil, then distilling in a column, heated to prevent obstructions, passing the vapours through heated towers filled with freshly ignited charcoal, and dehydrating by dry potash or soda. The ammonium carbonate is now condensed by cooling, and the remaining ammonia treated in the ordinary manner.

Saunders (U.S. P. 594100) describes his special apparatus for manufacturing ammonium carbonate.

Attempts have been made to obtain ammonium carbonate in the manufacture of ammonia-soda, not for commercial purposes, but in order to be used over again; *cf.* Lunge's *Sulphuric Acid and Alkali*, 2nd ed., vol. iii., p. 126. The results do not seem to have been very satisfactory.

Hempel (*Berl. Ber.*, xxi., p. 897) showed that ammonium carbonate (as well as chloride) can be reduced to hard lumps by compressing the powder very strongly at temperatures from 50° to 100° C. The process resembles the relegation of ice. It does not appear to be practically used.

Angelucci (*Gazz. chim. ital.*, vol. xlvi., p. 517) obtained ammonium carbonate by passing a mixture of acetylene and nitric oxide over platinum sponge, heated to 800° C., subsequently at once cooling down the gases to 100°. *Vide supra*, p. 844.

Lennard (B. P. 5603, of 1904), in order to obtain ammonium carbonate free from lead, makes the sublimers and condensers of aluminium.

Pure commercial ammonium carbonate (*cf.* its properties, pp. 954 *et seq.*) is quite white, and at a fresh fracture shining and transparent, but is soon covered in the air with a fine dust of ammonium bicarbonate, ammonia being given off. On being heated it should volatilize completely and without empyreumatic

smell; tarry matters are betrayed by a brown colour of the aqueous solution. The salt intended for analytical chemists should, after being neutralized with nitric acid, give no reaction with silver nitrate for chloride, or with barium salt for sulphate. Lime is indicated by a fixed residue and by precipitation with ammonium oxalate; lead (which should be avoided when the salt is to be employed as a baking-powder) by means of hydrogen sulphide. Sometimes thiosulphate is found by dissolving in acetic acid and adding silver nitrate, which produces a white precipitate, turning brown in a few moments.

This salt is principally employed for scouring wool, as a general detergent, in dyeing, as smelling-salts, as a baking-powder, in medicine, etc.

Ammonium Nitrite.

This salt is sometimes employed in the manufacture of explosives and for the preparation of nitrogen; for instance, for filling indiarubber balls. It can be prepared by double decomposition of lead nitrite and ammonium sulphate, as a crystalline mass, stable in the air. When slowly heated, it decomposes smoothly into nitrogen and water, $NH_4 . NO_2 = 2HO + 2N$; when quickly heated to 60° or 70° or by a blow, it decomposes with explosive violence.

Carez (Ger. P. 48278) manufactures it by reducing barium sulphate to sulphide in the usual manner and treating the solution with sodium nitrite. On evaporating the mixture and cooling, barium nitrite crystallizes out; the mother-liquor is boiled with sulphur, to convert barium hydrate into sulphydrate, which is equally decomposed with sodium nitrite. The barium nitrite is then decomposed with ammonium sulphate.

Ammonium Nitrate.

The following processes have been proposed for the manufacture of this salt, which is now used in considerable quantities for the manufacture of explosives.

Burghardt (B. P. 8841, of 1889) mixes equivalent quantities of the solutions of lead nitrate and ammonium sulphate. Or else (B. P. 5542, of 1890) he precipitates the solution of lead nitrate with liquor ammoniæ, or saturates it with gaseous NH_3;

the resulting white lead hydrochloride is to be converted into chrome-yellow.

The proposal of Gerlach and others for the manufacture of ammonium nitrate by the ammonia-soda reaction (*cf.* Lunge's *Sulphuric Acid and Alkali*, vol. iii., p. 155) is hardly practicable, owing to the incompleteness of the reaction. *Cf.* Chance's patent No. 5919, of 1885.

Roth (Ger. P. 48705) separates the products obtained by the interaction of ammonium sulphate and alkaline nitrates by means of alcohol. Or else (Ger. Ps. 53364 and 55155) he fuses equivalent quantities of ammonium sulphate and alkaline nitrate and heats to 160° or 200° C. for an hour, whereupon the liquid ammonium nitrate can be easily separated from the solid alkaline sulphate by centrifugalling or otherwise.

Benker (Ger. P. 69148) mixes equivalent solutions of ammonium sulphate and sodium nitrate, and allows to crystallize in the cold, whereby much Glauber's salt is formed and removed. The mother-liquor is treated with sufficient nitric acid to form (with the sodium sulphate) sodium nitrate and free sulphuric acid; and by cooling it down ammonium nitrate is made to crystallize out. The mother-liquor is used over again.

Fairley (B. P. 1667, of 1896) mixes 132 parts solid ammonium sulphate with 170 sodium nitrate, adds a little water, and heats to 108° to 110°, at which temperature the mixture is kept for 3 or 5 minutes. It now consists essentially of ammonium nitrate and sodium sulphate, and is extracted with methylated spirits of 85 to 93 per cent., containing ½ per cent. NH_3. The alcoholic solution contains ammonium nitrate with 10 per cent. sodium nitrate, the solid residue sodium sulphate with 8 per cent. ammonium sulphate.

The ammonium nitrate obtained from the alcoholic solution is purified by a special process. The mixed sodium and ammonium nitrates, after evaporation and recovery of the alcohol, are washed in an upright cylindrical vessel with cold water or a cold saturated solution of ammonium nitrate, which dissolves out the more soluble sodium nitrate. This process may be made continuous, and the moist ammonium nitrate, discharged from the top of the percolator, contains after drying less than 1 per cent. of impurities. The liquid from the per-

colator is evaporated to dryness, and the dry salts used over again in the next operation, as well as the ammonium sulphate recovered from its admixture with sodium sulphate by treatment with boiling water.

The same inventor (B. P. 1668, of 1896) describes a new form of the ammonia-soda process, working at −15°, for the manufacture of ammonium nitrate. Other patents have been taken out by Wahlenberg (No. 12451, of 1889), and by Groendahl & Landin (No. 1868, of 1892); but none of these, or the other alcohol processes, furnishes an article of sufficient purity for the manufacture of explosives, *i.e.*, containing less than 1 per cent. of solid impurities, as proved by Fairley (*J. Soc. Chem. Ind.*, 1887, p. 211).

Craig (B. P. 5815, of 1896; G. P. 92172) separates the mixture of ammonium nitrate and alkaline sulphates, obtained by the moistening of a mixture of alkaline nitrate and ammonium sulphate, stirring and drying, by means of liquid ammonia or most highly concentrated liquor ammoniæ, which dissolves only ammonium nitrate. For this he employs the apparatus shown in Fig. 305. An air-tight vessel, *a*, containing the filter *b*, is filled with the finely ground mixture of salts and digested with the liquid ammonia contained in vessel *l*, at as low a temperature as possible. The filtrate may be brought to 80 per cent. ammonium nitrate, but it is safer not to exceed 50 or 60 per cent., to avoid contamination with other salts. It is run through into *c*; the ammonia is aspirated away by pump *d*, liquefied in *c*, and passed into *a* by means of pipe *f*, and this is continued until the mass in *a* is exhausted. The latter is freed from ammonia by heating, and the white ammonium nitrate discharged by the manhole *i*. The vessels must be very strong, on account of the high pressure, and should be made of iron, enamelled or coated with tin or aluminium.

Lennox (B. P. 5483, of 1897; Ger. P. 96689) heats a dry mixture of 17 parts sodium nitrate and 13 ammonium sulphate in a retort, connected with a condenser and a scrubber, in a vacuum to such a temperature (not above 230°) that ammonium nitrate distils over, which commences at 200° C.; solid sodium sulphate remains behind. The retort is made of iron, the condenser of stoneware pipes. The vacuum is produced by an injector, and is made as high as possible. The nitric oxide

formed during the process is liquefied (?) on issuing from the condenser. The gases are washed in the scrubber with a concentrated solution of ammonium nitrate. In order to prevent stopping up the condenser with solid ammonium nitrate, a steam-jet is passed through it.

Garroway (B. P. 7066, of 1897) heats sodium nitrate with silica and steam; part of the nitric acid evolved is condensed; the remainder is made to meet NH_3 in plate towers, and the last NH_3 is retained by sulphuric acid.

Johnson (*Chem. Zeit.*, 1897, p. 527; Swed. P. 8944, of 1897)

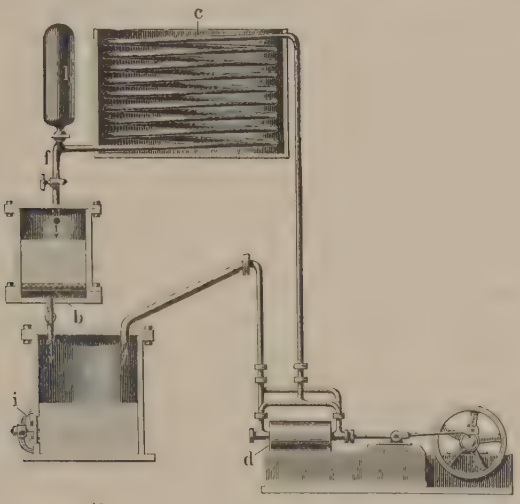


FIG. 305.

converts calcium superphosphate by ammonium sulphate and ammonia into ammonium phosphate, which is converted into nitrate by the action of sodium nitrate.

Rudeloff (Ger. P. 166427), in order to make ammonium nitrate free from nitrite, brings the nitric acid, as obtained in denitrating processes, into direct contact with gas-liquor.

Feld (Ger. P. 177172) produces ammonium nitrate by the action of the gases of coal-distillation, containing NH_3 and CO_2 on solutions of alkalis or alkaline nitrates. According to his Ger. P. 178620, he first removes the H_2S from such gases

by suitable means. His B. P. is No. 5776, of 1906; U.S. P. 839741.

Naumann (Ger. P. 166746) promotes the old reaction between ammonium sulphate and sodium nitrate by separating the sodium sulphate formed from the mother-liquor while still hot; the solution is then cooled to the point where only a double sulphate of ammonium and sodium crystallizes out, and the mother-liquor, on concentration and cooling, yields solid, nearly pure, ammonium nitrate. The process of R. Wedekind & Co. (G. P. 184144; B. P. 19465, of 1906; Fr. P. 369389; U.S. P. 864513) runs quite on the same lines, but they add in the end so much water, that the sodium salts remain in solution, and only pure ammonium nitrate crystallizes out. They proceed as follows. A solution is made of 400 parts ammonium sulphate and 720 sodium nitrate (=40 per cent. excess) in 900 water, and is heated till it shows a boiling-point of 118°, at which point most of the sodium sulphate has been precipitated. The liquid is filtered and boiled down, until a sample cooled down to 70° begins to separate ammonium nitrate. It is then cooled down to about 70°, the salts separating thereby (sodium nitrate and sulphate) are removed and so much water is added to the mother-liquor that, on cooling down to 15°, the sodium salts remain in solution. The liquor thus diluted is cooled down to 15°, whereupon about 40 per cent. of the ammonium nitrate crystallizes out, free from sodium salts. The crystals are freed from the mother-liquor adhering to them by washing with a solution of ammonium nitrate. All the liquors go back to the next process.

Garroway (B. P. 10137, of 1899) first obtains strontium nitrate from sodium nitrate and strontium chloride (most of the NaCl separating out on cooling), and after purifying it by recrystallization, adds the exactly equivalent quantity of ammonium sulphate. The latter is converted into nitrate and remains in solution. All the strontium is precipitated as sulphate, which is converted into carbonate by means of sodium carbonate, and from the $SrCO_3$ the $SrCl_2$ is again prepared by means of hydrochloric acid.

According to the German patent of the Norsk Hydro-Elektrik Kvaelstofaktieselskab, No. 206949, of 1907, ammonium

nitrate is obtained, together with calcium nitrate, by absorbing nitrous vapours by calcium cyanamide, the reaction taking place quite smoothly according to this equation :—

$$CaCN_2 + 2H_2O + 4HNO_3 = Ca(NO_3)_2 + CO_2 + 2NH_4 . NO_3$$

Ammonium Persulphate.

This salt has been recently introduced into trade, *e.g.*, for photographic purposes. It is always made by electrolysis of an acid solution of ammonium sulphate. According to a Ger. P. (195811) of the Consortium für Elektrochemische Industrie at Nürnberg, it is made by electrolyzing a saturated solution of ammonium sulphate, containing free acid, without a diaphragma, with a cathodic current-density of at least 20 amperes per superficial decimeter, without adding any chromium compounds (as had been previously done). The free acid must always prevail, so that even in the immediate neighbourhood of the cathode no layer with alkaline reaction is formed. The yield, which at 10 amperes per square decimeter is about 25 per cent., at 50 amperes rises to 50 per cent., at 150 amperes to 60 per cent., and at 300 amperes to 70 per cent. of the equivalent of the current. The process has the advantage of going on at a low temperature, without specially prepared electrodes and of yielding a product not contaminated by chromium compounds.

Ammonium Perchlorate.

Alvisi (Ger. P. 103993) makes this by treating a concentrated solution of 273 parts of sodium perchlorate with a strong solution of 75 to 77 parts of ammonium nitrate. The ammonium perchlorate is precipitated in the form of small crystals, which are treated in a hydro-extractor or pressed, and then recrystallized.

Ammonium Thiosulphate.

The Chemische Fabrik auf Aktien vorm. E. Schering (Ger. Ps. 202502 and 202503) prepare that salt, which is employed in photography for fixing the halogen compounds of silver, by mixing ammonium chloride (or sulphate or oxalate) with a concentrated solution of sodium thiosulphate, heating to about 100° C. and separating at this temperature, by means of a heated pressure-filter, the solution from the fixed salts, which contain

80 to 85 per cent. sodium chloride. A most highly concentrated solution is obtained by introducing finely ground ammonium chloride into sodium thiosulphate, fused in its water of crystallization, and thoroughly stirring at a temperature of 95° to 100° C.

Ammonium Phosphate.

Both the acid phosphate or monammonium phosphate ($NH_4H_2PO_4$), and the intermediate phosphate, or diammonium phosphate, $(NH_4)_2HPO_4$, are commercial products.

According to Lagrange,[1] these salts are made from superphosphate, manufactured in the usual way by treating mineral phosphates with sulphuric acid. This product is lixiviated with water and with the aid of steam injected into the mixture, in a methodical way, whereby liquors of 25° Bé. (=42° Tw.) are obtained. The residue, consisting principally of calcium sulphate, is thrown away. The solution contains free phosphoric acid, monocalcium phosphate, calcium sulphate, and a little free sulphuric acid. First the latter is removed by adding a slight excess of barium carbonate; the precipitated barium sulphate is separated by filtration and can be utilized as a paint. The filtrate, which now contains only phosphoric acid, monocalcium phosphate, and very little monobarium phosphate, is neutralized by ammonia in slight excess. This precipitates all the lime as basic phosphate, which is washed and used over again, along with the native phosphate, for manufacturing superphosphate. The filtered solution contains monammonium (acid) phosphate and will test about 20° Bé. (=32° Tw.). It should be at that concentration to effect the precipitation of the biammonium phosphate, in the following manner:—The above liquor and liquor ammoniæ (of 22 Bé.=0·921) are gradually mixed in small vessels, in the proportion of $1\frac{1}{2}$ equivalents of NH_3 to 1 equivalent of monammonium phosphate. The biammonium phosphate at once separates out as a crystalline mass; but the vessels must be closed, to prevent the escape of ammonia, which is all the more likely to take place, as the reaction produces a rise of temperature. After cooling, the contents of the vessels form a thick paste, which is submitted to hydraulic pressure. The mother-liquor is used for the manufacture of ammonia; the cakes consist of pure

[1] Vincent, *Industrie des Produits ammoniacaux*, p. 104.

$(NH_4)_2HPO_4$, and are sold to those sugar-refiners who employ the purifying-process of Lagrange.

Ammonium Chromates.

The normal chromate, $(NH_4)_2CrO_4$, is not of technical importance, but the bichromate, or rather pyrochromate, $(NH_4)_2Cr_2O_7$, and the trichromate, $(NH_4)_2Cr_3O_{10}$, have been introduced into the manufacture of explosives. The *bichromate* forms easily soluble, garnet-red monoclinic crystals; lighted at one point, the salt is quickly decomposed all through with fiery glow, and leaves green chromium oxide. The *trichromate* is prepared from the former salt by the action of nitric or chromic acid. It forms dark red rhombic prisms, very easily soluble in water, with liberation of chromic acid; at 110° or 120° they assume a dark brown colour, and later on they deflagrate violently, leaving black chromium oxide.

The United States Smokeless Powder Co. (B. P. 10684, of 1894) prepares these chromates by mixing concentrated solutions of sodium chromates and ammonium picrate; the sodium picrate, which is very little soluble, is separated by crystallization.

Ammonium Acetate.

The *neutral* salt, $NH_4,C_2H_3O_2$, forms deliquescent needles, losing ammonia when heating the aqueous solution to 55°. The anhydrous salt fuses at 89°, being decomposed into ammonia, acid salt, and acetamide.

The *acid* salt, $NH_4,Ca_2H_3O_2+C_2H_4O_2$, is more stable and can be sublimed at 120°. It is deliquescent in the air and is soluble in alcohol.

W. Smith (B. P. 18693, of 1891) manufactures ammonium acetate from crude grey acetate of lime by dissolving this in a little water, settling, mixing the clear solution with more than its equivalent of a concentrated solution of sodium sulphate, filtering the solution of sodium acetate from the gypsum formed, evaporating to dryness, distilling the dry salt with sulphuric acid, neutralizing the distilled acetic acid with lime, evaporating the solution, heating the pure calcium acetate formed with a solution of ammonium sulphate to 60° or 80°, and separating the solution of ammonium acetate from the calcium sulphate.

APPENDIX

Tables I., II., III.

(For reducing the specific gravities of liquids lighter than water to the normal temperature of 15·5 C.,=60° F.)

Note.—The scale of reduction is not the same for high and low temperatures; hence three tables are given. When the observed temperature is *below* the normal, the figures in the table must be *deducted* from the observed specific gravity in order to reduce this to the normal temperature, and *vice versâ*.

I. For Specific Gravities of 0·880 downwards.

Degrees C. .	·2	4	6	8	10	12	13½	15½
Deduct .	0·0105	0·009	0·008	0·006	0·0045	0·003	0·002	0

Degrees C. . . .	17½	19½	21½	23	25	27	29
Add . . .	0·100	0·0025	0·004	0·0055	0·007	0·008	0·010

II. For Specific Gravities between 0·880 and 0·920.

Degrees C. . .	2	4	5½	7	9	10½	12	14
Deduct . .	0·010	0·0085	0·0075	0·0065	0·005	0·004	0·001	10·00

Degrees C. . .	15½	17	19	20½	22	24	25½	27	29
Add . . .	0	0·001	0·0025	0·0035	0·005	0·006	0·007	0·008	0·0095

III. For Specific Gravities between 0·920 and 0·960.

Degrees C.	1½	3	4½	6	7	8½	10	11½	13	14	15½
Deduct .	0·010	0·009	0·008	0·007	0·006	0·005	0·004	0·003	0·002	0·001	0

Degrees C.	17	18	19½	21	22½	24	25	26½	28	29½
Add. .	0·001	0·002	0·003	0·004	0·005	0·006	0·007	0·008	0·009	0·010

Table IV.

(For comparing the degrees of Baumé's, Cartier's, and Beck's hydrometers with the corresponding specific gravities, for liquids lighter than water.)

Degrees.	Baumé.	Cartier.	Beck.	Degrees.	Baumé.	Cartier.	Beck.
0	...	...	1·0000	17	0·952	0·955	0·9090
1	...	...	0·9941	18	0·946	0·948	0·9042
2	...	...	0·9883	19	0·940	0·941	0·8994
3	...	...	0·9826	20	0·933	0·934	0·8948
4	...	...	0·9770	21	0·927	0·928	0·8900
5	...	...	0·9714	22	0·921	0·921	0·8854
6	...	...	0·9659	23	0·915	0·914	0·8808
7	...	...	0·9604	24	0·909	0·908	0·8762
8	...	...	0·9550	25	0·903	0·901	0·8717
9	...	...	0·9497	26	0·898	0·995	0·8673
10	1·000	...	0·9444	27	0·892	0·889	0·8629
11	0·993	1·000	0·9392	28	0·886	0·883	0·8585
12	0·986	0·992	0·9340	29	0·881	0·877	0·8542
13	0·979	0·985	0·9289	30	0·875	0·871	0·8500
14	0·972	0·977	0·9239	31	0·870	0·865	0·8457
15	0·966	0·970	0·9189	32	0·864	0·859	0·8415
16	0·959	0·962	0·9139				

Table V.

(For comparing the degrees of the Centigrade and Fahrenheit Thermometers.)

C.	F.	C.	F.	C.	F.	C.	F.
+500	+932	+74	+165·2	+45	+113	+16	+60·8
400	752	73	163·4	44	111·2	15	59·0
300	572	72	161·6	43	109·4	14	57·2
200	392	71	159·8	42	107·6	13	55·4
100	212	70	158	41	105·8	12	53·6
99	210·2	69	156·2	40	104	11	51·8
98	208·4	68	154·4	39	102·2	10	50·0
97	206·6	67	152·6	38	100·4	9	48·2
96	204·8	66	150·8	37	98·6	8	46·4
95	203	65	149	36	96·8	7	44·6
94	201·2	64	147·2	35	95	6	42·8
93	199·4	63	145·4	34	93·2	5	41·0
92	197·6	62	143·6	33	91·4	4	39·2
91	195·8	61	141·8	32	89·6	3	37·4
90	194	60	140	31	87·8	2	35·6
89	192·2	59	138·2	30	86	1	33·8
88	190·4	58	136·4	29	84·2	0	32·0
87	188·6	57	134·6	28	82·4	−1	30·2
86	186·8	56	132·8	27	80·6	2	28·4
85	185	55	131	26	78·8	3	26·6
84	183·2	54	129·2	25	77·0	4	24·8
83	181·4	53	127·4	24	75·2	5	23·0
82	179·6	52	125·6	23	73·4	6	21·2
81	177·8	51	123·8	22	71·6	7	19·4
80	176	50	122	21	69·8	8	17·6
79	174·2	49	120·2	20	68·0	9	15·8
78	172·4	48	118·4	19	66·2	10	14·0
77	170·6	47	116·6	18	64·4	11	12·2
76	168·8	46	114·8	17	62·6	12	10·4
75	167						

All the temperatures mentioned in this book are in Centigrade degrees, but can be converted into Fahrenheit degrees by means of the above table.

ADDENDA

Page 15. *Statistics on the Production of Coal-tar and Coal-tar Products in the United States.*—According to the *Thirteenth Census Bulletin*, the quantities produced in 1900 and 1905 in the United States were as follows (the unit employed is the short ton of 2000 lb. = 0·89285 long ton):—

	1900.	1905.	
Coal-tar	67,094	77,643	short tons.
Water-gas tar	222,868	259,934	„
Coke-oven tar	52,344	(?)	
Pitch	...	61,100	„
Refined coal-tar	...	577,650	gallons.
Creosote oil	...	288,817	„
Other tar oils	...	17,175	short tons.
Coal-tar worked up (not burned)	110,023	127,756	„
Possible production of tar from the coke produced, if this were done in by-product ovens	...	1,476,306	„
Tar and pitch imported	...	46,057	barrels.

Page 36. *Promoting the Separation of Tar from the Hot Gases of Destructive Distillation.*—The firm Dr C. Otto & Co. (Ger. Ps. 203254 and 204570) introduces the tar by means of a tar-spray jet, which at the same time produces the movement of the gases. Thus the hot gases, after being freed from tar, can be immediately passed into the acid intended for absorbing the ammonia. A jet of thin tar is introduced into the gas previously to the tar-spray blower, which process has the advantage of washing any lumps of tar, retained in the thick-tar blower, out of the latter.

Burstell (B. P. 10901, 1908) describes a washer or cooler for

the purpose of depriving gases of tar and dust, and for cooling the gas.

Pages 80 and 106. *Condensation of Tar from the Gases obtained in the distillation of Coal.*—Dr C. Otto & Co. describe further improvements of their process in their Ger. P. 204576, issued in 1909.

Körting Brothers (Ger. P. 204888) put gas-tight iron tanks for the condensed tar and ammonia into connection with a pipe conducting coal-gas into the tanks, in order to prevent the entrance of atmospheric air, which would cause corrosion of the iron.

Page 103. *Recovery Coke-ovens.*—Further patents have been taken out by T. von Bauer (Fr. P. 390720; *J. Soc. Chem. Ind.*, 1908, p. 1103); by Kros (Fr. P. 391228; *eod. loco*); by D. Wright (B. P. 13292, of 1907; *J. Soc. Chem. Ind.*, 1907, p. 742).

Page 149. *Production of Benzene or its Homologues from Petroleum.*—Starke (U.S. P. 913780) treats the "distillate of petroleum, which contains a benzene nucleus," by agitating and heating with concentrated sulphuric acid, until the evolution of sulphur dioxide ceases. The mass is then allowed to settle until the sulphonic acids have separated from the petroleum and the benzene is recovered from the sulphonic acids by distillation.

Page 174, lines 1 and 2 from the bottom, and page 174, lines 1 to 6, should be behind Crotonylene on page 176.

Page 175, lines 7 to 13 belong to page 174, behind the paragraph "Crotonylene," with the title, "Valylene."

Page 177. *History of Benzol* (*benzene*).—Schelenz (*Z. angew. Chem.*, 1908, p. 2577) shows that the compound which we now term "benzol," or more recently "benzene," has been discovered in coal-tar forty years before Faraday in 1825 reported "On new compounds of carbon and hydrogen, and on certain other products obtained during the decomposition of oil by heat." In Macquer-Leonhardi's *Chymisches Wörterbuch*, published at Leipzig in 1783, vol. i., pp. 86, 709, a passage is found which in English translation runs as follows:—"From coal we can obtain by distillation a nearly tasteless water, a brownish-yellow, disagreeably balsamically smelling oil, and another empyreumatic,

tougher oil which can be rectified into naphthol (that is, 'mountain-oil,' in the old classic sense), like petroleum." In 1784 was published at Leipzig, *Demachy's Laborant*, translated into German by Samuel Hahnemann, in which the distillation of coal on the large scale is described, enumerating the various fractions, one of which can be at once put into bottles in which a space of at least 3 or 4 fingers' breadth must be left. Even before this, in Caspar Neumann's *Praelectiones Chemicæ*, published at Schneeberg in 1740, it is stated that "fossile carbons" on distillation yield a little water and "a sharply tasting spirit," which must have been benzol. Mitscherlich called the substance which he obtained in 1833 on the distillation of benzoic acid with lime, "benzin." It is not quite certain whether the designation "benzol" was first used by Faraday or by Liebig; "benzène" appears in French publications of 1861. In the same year Hirzel recommended "benzol from coal-tar," mixed with magnesia as a detergent. Confusions with "benzin" from petroleum were still very frequent, until for Germany the official *Deutsches Arzneibuch* in 1882 made a definite distinction between "benzinum petrolei" and "benzol from coal-tar." This is practically the same distinction as is made in England.

The term "benzene" is everywhere understood to mean the *pure* compound C_6H_6, for which, however, the designation "benzol" is also frequently employed, *e.g.*, in the pharmacopœia. "Benzin" is reserved for the quite different hydrocarbons distilled from petroleum.

Page 182, line 10, in lieu of p. 1527 read: I., p. 527.

Page 195. *Fluorene.*—The Gesellschaft für Teerverwertung in Duisburg (Ger. Ps. 203312 and 209432) obtains fluorene from mixtures with other substances by transforming it into an alkaline compound which can be separated from unchanged hydrocarbons. This is done by a treatment with sodium, preferably in the presence of a small quantity of organic bases, like aniline, benzylamine, or pyridine, and their homologues, which seem to act as contact substances.

Indene (*cf.* p. 189) is obtained in a similar manner, according to Ger. Ps. 205465 and 209694 of the same firm.

Page 225. *Diphenylene Oxides.*—The treatment of *o*-diphenol,

obtained in the production of anthracene and of fluorene, is the subject of the Ger. Ps. 111359, 124150, and 130679 of the Aktien-Gesellschaft für Teer- und Erdöl-Industrie (*Cf.* Weger, *Z. angew. Chem.*, 1909, p. 392).

Page 228. *Bases in Coal-tar.*—Trobridge (*J. Soc. Chem. Ind.*, 1909, xxviii., p. 230) describes the basic compounds found in tar from Otto-Hilgenstock coke-ovens.

Page 231. *Properties of Pyridine.*—K. Mackenzie (*J. Ind. and Eng. Chem.*, 1909, p. 360) states that commercial pyridine always contains picolines and water. The latter forms with pyridine a definite hydrate, boiling at 94°·4 C. This hydrate has very little solvent action on bituminous matters, and its presence materially impairs the solvent powers of pyridine. The picolines are even better solvents than pyridine, and in some cases surpass even carbon bisulphide in that respect.

Page 232. *Lutidines* (*Dimethylpyridines*) *in Coal-tar.*—Ahrens & Garbow (*Ber.*, 1904, p. 2062) found in the fraction of coal-tar bases boiling at 160 to 165° α, β' dimethylpyridine, in the fraction 165° to 170 β, β' and α, χ dimethylpyridine (previously found therein by Lunge and Rosenberg, as quoted in the text).

Page 305. *Manufacture of Lampblack from Coal-tar Pitch and the like.*—The Rütgerswerke A.-G. (Ger. P. 208600) improve the yield of lampblack, which hitherto amounted to 20 to 25 per cent. from tar, or 12 to 15 per cent. from pitch, 50 to 60 per cent. remaining as coke in the fireplace. It is better to extract the tar or pitch by suitable solvents—*e.g.*, naphthalene—to separate the remaining carbon from the solution, and to work the latter either as a whole, or after volatilizing the solvent, for lampblack by inflammation in the usual manner.

Page 322. *Removal of Free Carbon from Tar.*—Nikiforoff (Ger. P. 143549) employs a water-cooled tank provided with a partition and a stirrer at the bottom of this. This tank is filled with tar. The products of dry distillation are forced through this, and here yield their free carbon to the tar; the temperature being kept at about 170 , everything volatile at that temperature escapes and is condensed in the usual manner.

Page 350. *Explosions by the employment of air-pressure for moving tar oils* have been observed by Klocke (*Chem. Zeit.*,

1905, p. 725). This happened in several cases where hot oils, serving for the extraction of benzol from coke-oven gases, were repeatedly moved about under a pressure of from 2 to 4 atmospheres. The cause of this seems to be the gradual formation of sulphurets of iron, which may inflame already at a temperature of 120° or 123° C. This has caused many factories to abstain from the use of air-pressure for that purpose. If the air contains at least 12 or 13 per cent. CO_2 (say, in the shape of cold combustion gases), no such danger would exist.

Page 355. *Preventing the Boiling-over of Tar-stills.*—Ostrejka (*Vafta*, 1908) treats tar, containing water and therefore liable to boiling-over, with superheated steam, gradually going up to the temperature of melting tin (228° C.).

Page 468. *Testing the Consistency of Bituminous Binders in the Asphalt Paving Industry.*—An apparatus for this purpose has been constructed by C. N. Forrest, and is made by Howard & Morse, Brooklyn, N.Y. It consists of an aluminium saucer and a conical brass collar, which is filled with the bitumen under examination. The whole is immersed in water of 90° F., and the number of seconds is noted which elapses until the mass has been forced out of the collar and the apparatus sinks below the surface.

Page 468. *Melting-point of Pitch.*—E. A. Kolbe ("Inaugural Dissertation," Zürich, 1908) ascertained the melting-points of ten samples of French coal-tar pitches (sp. gr. 1·252 to 1·271) by Kraemer and Sarnow's method, as described in the text, and found them to range between 105° and 129° C.

Page 470. *Distinguishing Natural Asphalt from Tar Asphalt.*—A committee of the International Congress for the Examination of Technical Materials, of which G. Lunge was appointed President, reported to the Congress held at Brussels in 1906 on the above subject. The principal contribution to it was an investigation by Lunge and Krepelka on a number of natural and artificial asphalts. The specific gravities of coal-tar pitches, both soft and hard (1·23 to 1·27), are much above those of natural or petroleum asphalts (0·98 to 1·17). The fusing-points are too irregular to allow of any use for distinguishing both kinds of asphalt. The specific gravities of the solutions in

chloroform are distinctly higher for coal-tar pitch than for natural asphalt, and so are the "iodine numbers" in both cases (*Chem. Zeit.*, 1904, xvi., p. 177; *Z. angew. Chem.*, 1904, p. 1116).

Pages 526 and 538. *Antiseptic Properties of Phenols and of indifferent Tar Oils.*—Seidenschnur (*Chem. Zeit.*, 1909, p. 701) asserts that the phenols possess antiseptic properties only in aqueous solution, but not when dissolved in tar oils, in the shape of cresote oil, etc. Coal-tar oils, after being deprived of phenols, have exactly the same bactericidal action as before. The antiseptic properties of anthracene oil are even superior to those of lower-boiling tar oils. Petroleum oils have no antiseptic power unless a little sulphur has been dissolved therein in the state of boiling.

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